

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

JUNE 1929.

CXXV. *The Constitution and Density of Particles in Precipitated Smokes.* By H. P. WALMSLEY, M.Sc.*.

THIS paper describes the results obtained from X-ray data for particles in electrically precipitated smokes which were produced by the volatilization of metals from an electric arc in air. The precipitates form bulky flocculent powders. The best-known example, although not usually prepared in this way, is the deposit from a zinc oxide smoke—the so-called “philosophers’ wool.” The colour, appearance, and general properties of many of the precipitates have been described by Kohlschütter and Tüscher⁽¹⁾, who incidentally give values of the density in bulk of some of them. The results come out much less than the normal densities of the material of which they are composed, *e.g.*, values of 0·83, 0·56, 0·46 were obtained for the smoke of lead monoxide, the normal density of which is 9·6.

Indirect measurements of the density of individual particles actually in suspension in a smoke have been made by various observers with similar results. Meyer and Gerlach⁽²⁾ measured the rate of fall of a given particle at various gas pressures, and found that they could only make their results self-consistent by assuming a density of 11·56 for particles from platinum, the normal density of which is 24·1. Bär⁽³⁾, using the same method, obtained similar results and concluded that the particles were not homogeneous but possessed

* Communicated by Prof. W. L. Bragg, F.R.S.

either a sponge-like structure or an irregular non-spherical shape. The validity of the deduction was disputed on theoretical grounds by Sexl⁽⁴⁾. Patterson and Whytlaw-Gray⁽⁵⁾ used the method devised by Ehrenhaft and Millikan for the determination of the electronic charge, to measure the densities of individual particles in smokes from various substances dispersed in air. As an example, particles from silver ($\rho=10.5$) gave values ranging from 4.22 to 0.64. Here again it was considered that the particles on which measurements were made were agglomerates of smaller units loosely held together, and that the values obtained were averages for heterogeneous aggregates. With the necessary changes, the objections of Sexl may be directed equally against these results.

The question of the constitution of a smoke particle involves two distinct problems—the nature of the ultimate units from which the particle is built and the manner in which the units are assembled. The present work is an attempt to solve the first only of these problems, but it gives a hint as to the probable solution of the other. We may anticipate the results by saying that the ultimate units prove to be crystalline particles of the normal density of the material of which they are composed. The general conclusions of Bär and Patterson and Whytlaw-Gray are therefore supported. It seems probable that the particles they examined in many cases were really crystal aggregates. The observations of Kohlschütter and Tüscher are easily explained. Briefly, the relation between philosophers' wool and zincite—the crystallized form of zinc oxide—is analogous to that between snow and ice.

Experimental Method.

The smokes were produced by striking an electric arc in air between electrodes of various common metals. A large inverted funnel was placed immediately over the electrodes. The smokes were drawn from this by suction through a long glass tube of about 2 cm. diameter, lined with a loose sheet of aluminium foil, and which contained a central insulated brass rod. The latter was charged to a high potential by means of an influence machine. The foil was earthed. This constituted the precipitator. The smoke particles collected both on the foil and on the central rod, and when sufficient material had accumulated the precipitated powder was collected from both, placed in a tube, and tightly corked until required for analysis. The metals used were as found

in the laboratory: they were not specially selected substances of a high degree of purity.

The material was analysed by the powder method, using a camera of about $3\frac{1}{2}$ in. diameter. In most cases copper $K\alpha$ radiation was employed. The lattice constants were deduced from the measurements of glancing angle θ by means of the general formula

$$\sin^2 \theta = Ak^2 + Bk^2 + Cl^2 + Dhk + Ehl + Fkl, \quad (1)$$

where h, k, l are the indices to the planes, using the method of successive approximations. The densities were then computed from the formula

$$\rho = 1.65 \times 10^{-24} nM/\text{volume of unit cell}, \quad (2)$$

where n is the number of molecules in the cell and M their molecular weight, calculated to $O=16$.

It is somewhat difficult to assign limits to the accuracy of the values of ρ deduced from the measurements, although it seems unlikely that many are greater than 1 per cent. in error. The accuracy of the deduced lattice constants not only depends upon the number of variables involved in equation (1), but it also depends upon the number and sharpness of the lines available for measurement. The breadth of the spectrum line is a function of the average size of the particles which produce it. Silver, for example, gave quite sharp lines, whilst the sample of platinum, which produces a similar pattern, gave relatively broad and diffuse lines. The error on this account in the deduced constant is probably less for silver than for platinum where the particles were finer. It should also be remembered that the experimental values given are individual results which have not been examined for accidental and systematic errors. The fact that the observed value $a=4.203$ Å. for magnesium oxide happens to be identical with the value given by Wyckoff in the International Critical Tables should not be taken as evidence in support of the tabulated value as against the value $a=4.208 \pm .001$ recently proposed by Broch⁽⁶⁾. The interpretation to be put upon the result is that the crystals in the precipitated smoke have, apparently, an internal structure and a density identical with the crystals used by Broch and the authorities quoted by Wyckoff.

Experimental Results.

The precipitates with one exception proved to be crystalline. Many of the individual results call for little comment.

As was previously known, the readily oxidizable metals give oxides, whilst platinum, silver, and gold give metallic smokes. Magnesium, cobalt, nickel, and cadmium give the simple face-centred cubic monoxides. The deposit from calcium, which was dispersed by Kohlschütter's⁽¹⁾ method from the crater of a carbon arc, contained calcium monoxide and calcium hydroxide. Evidently the smoke dispersed was the monoxide which subsequently absorbed moisture from the air passing through the precipitator during the time involved in collecting the material. Thallium and chromium gave sesquioxides. The former was cubic and the latter the rhombohedral crystal of the α corundum type. Zinc gave the hexagonal monoxide.

The remaining substances may be classified roughly into two groups: smokes which contained more than one substance in the disperse phase and the interesting group which contained oxides possessing polymorphous crystalline modifications. Silver, iron, and copper gave smokes falling in the first group, and aluminium, arsenic, antimony, lead, and carborundum (from which silica is dispersed by Kohlschütter's method) gave oxides of the second group. These smokes are described in greater detail in what follows. The experimental data are collected in Table I.

Silver.—Although silver and platinum both produce metallic smokes, the dispersal process seems more than simple volatilization succeeded by condensation. One smoke from silver was dispersed from electrodes which consisted of pieces of silver about 1 cm. long by 0.5 cm.² in cross-section, mounted on brass rods. During dispersal, the silver ends kept at a red heat. On analysis, the smoke produced gave only lines due to metallic silver. Another smoke was dispersed from electrodes which consisted of silver-foil rolled into the form of a rod. This arc was more difficult to maintain—it ran intermittently and the electrodes obviously kept at a lower average temperature. In addition to metallic silver, the smoke in this case was found to contain a proportion of silver oxide Ag_2O .

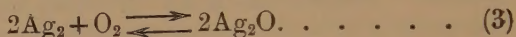
Now von Wartenberg⁽⁷⁾ has shown, from vapour pressure measurements at high temperatures, that silver is more readily volatilized in oxygen than in hydrogen or nitrogen, and in consequence apparently possesses a higher vapour pressure in oxygen than in the other gases. This he attributes to the intermediate formation of an oxide in the silver vapour, which immediately decomposes again. He actually found traces of oxide in samples of silver distilled

TABLE I.

No.	Metal Used.	Material Dispersed.	Crystal System.	Unit Cell in Å.			Calculated Density.	Comparison Data.			Ref.
				a.	b.	c.		a.	b.	c.	
1	Mg	MgO	C	4.203	—	—	3.583	4.203	—	—	W* (22)
2	Al	$\left\{ \begin{array}{l} \text{Al}_2\text{O}_3 \beta \\ \text{Al}_2\text{O}_3 \end{array} \right\}$	H	5.591	—	22.71	3.290	5.63	—	22.63	—
3	SiC†	SiO ₂	—	—	—	—	—	—	—	—	—
4	Ca†	$\left\{ \begin{array}{l} \text{CaO} \\ \rightarrow \text{Ca}(\text{OH})_2 \end{array} \right\}$	C	4.801	—	—	3.343	4.79	—	—	(20)
5	Cr	Cr ₂ O ₃	H	3.588	—	4.922	2.226	3.52	—	4.93	W
6	Mn†	Mn ₂ O ₃	Tet	4.946	—	13.55	5.238	4.94	—	13.57	W
7	Fe	$\left\{ \begin{array}{l} \text{Fe}_2\text{O}_3 \alpha \\ \text{Fe}_2\text{O}_3 \gamma \end{array} \right\}$	H	8.149	—	9.448	4.709	8.14	—	9.42	(23)
8	Co	CoO	C	5.031	—	13.74	5.247	5.03	—	13.74	W
9	Ni	NiO	C	8.366	—	—	5.400	8.37	—	—	W
		CuO	Tri	4.247	—	—	6.455	4.24	—	—	W
				4.171	—	—	6.79	4.172	—	—	W
				3.74	4.67	4.67	6.503	3.74	4.67	4.67	W
				85° 21'	β 86° 25'	γ 93° 35'	—	85° 21'	β 86° 25'	γ 93° 35'	W
10	Cu	Cu ₂ O	C	4.254	—	—	6.132	4.28	—	—	W
11	Zn	ZnO	H	3.250	—	5.217	5.623	3.25	—	5.23	W
12	As	As ₂ O ₃	C	11.05	—	—	3.869	11.06	—	—	W
13	Ag	Ag ₂ O	C	4.077	—	—	10.50	4.079	—	—	W
14	Cd	CdO	C	4.747	—	—	7.14	4.72	—	—	W
15	Sn	$\left\{ \begin{array}{l} \text{SnO}_2 \\ ? \end{array} \right\}$	Tet	4.687	—	—	8.226	4.72	—	—	W
				4.747	—	3.188	6.915	4.72	—	3.16	W
16	Sb	Sb ₂ O ₃	R	12.00	3.347	—	—	—	—	—	(18)
17	W	WO ₃	R	7.336	10.48	8.489	5.578	—	—	—	(25)
18	Pt	Pt	C	3.914	—	4.18	7.146	—	—	—	W
19	Au	Au	C	4.065	—	—	21.47	3.913	—	—	W
20	Tl	Tl ₂ O ₃	C	10.53	—	—	19.37	4.064	—	—	W
21	Pb	PbO	R	5.467	4.742	—	10.31	10.57	4.72	5.880	(26)
						5.862	9.688	$\left\{ \begin{array}{l} 5.50 \\ \pm .02 \end{array} \right\}$	$\left\{ \begin{array}{l} 4.72 \\ \pm .03 \end{array} \right\}$	$\left\{ \begin{array}{l} 5.880 \\ \pm .003 \end{array} \right\}$	
22	Bi	Bi ₂ O ₃	Tet	5.462	—	5.619	9.128	—	—	—	(25)

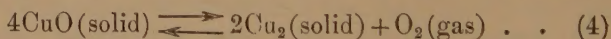
* The reference W is to Wyckoff, "X-ray Diffraction Data," International Critical Tables, vol. i. 1926.
 † Dispersed from the crater of a carbon arc.

in oxygen, which supports the hypothesis. The formation of a silver smoke in air, therefore, seems to involve the equilibrium of a system which perhaps may be represented by the reaction

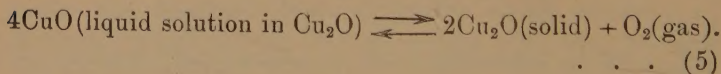


Since the oxide is decomposable by heating, we should expect the reaction to move towards the left at high temperatures. At the temperature of the silver-foil arc, the equilibrium amount of oxide will be greater than at the red heat of the metallic arc. Thus the difference in the compositions of the two smokes seems explicable if we suppose that the disperse system is formed at a temperature approaching that of the arc and that the equilibrium proportions of the solid phases are at least partially conserved by the quenching action of the air currents which flow past the electrodes when the arc is running.

Copper.—An analogous effect is found with copper. The copper arc gave a mixture of cupric oxide and cuprous oxide. The former seemed in excess. In addition, there were a few faint lines on the film which were not identified. The equilibrium of the system cupric oxide, cuprous oxide, oxygen, has been studied in detail by Smyth and Roberts⁽⁸⁾. It has a eutectic point at $1080^{\circ}\cdot 2$ C. and at 402·3 mm. pressure, where four phases are in equilibrium, both solid oxides, oxygen gas, and a liquid eutectic of both oxides. At lower temperatures both oxides remain solid and the reaction



takes place. At higher temperatures and at pressures less than 402·3 mm. fusion occurs and the reaction is



The dissociation pressure of reaction (4) at 1026° C. and of reaction (5) at 1135° C. is equal to 153 mm., the partial pressure of oxygen in air. If, therefore, the smoke particles are formed by a condensation process (the usual assumption), and we may further assume that when formation occurs the medium has the same oxygen content as normal air, some of the particles must have formed at a temperature higher than 1026° C., the temperature at which cupric oxide begins to dissociate when heated in air. The presence of cuprous oxide in the smoke shows that the subsequent cooling of the disperse system, as its temperature fell below 1026° C. where

reaction (4) proceeds from right to left, must have been rapid. The particles were quenched before the reaction could pass to completion.

Thus the nature of the material dispersed from a copper arc depends upon the temperature at which the particles are formed and the partial pressure of the oxygen present in the medium on formation*. When the latter is 153 mm. it is clear that below 1026° C. we should obtain a smoke of cupric oxide particles only. Temperatures between 1026° C. and 1135° C. are required to produce cuprous oxide and with temperatures greater than 1135° C. we may get solidified particles from the phase represented by the left-hand member of equation (5). These particles may be responsible for the weak unidentified lines in the spectrum of the precipitated smoke. It seems clear that the actual formation of the particles as a disperse system occurs at a high temperature and close to the electrodes of the arc. But the temperature of the arc is known to vary at different parts, so even if, as it seems probable from their small mass, the particles on formation are in thermodynamical equilibrium with the adjacent medium, it is impossible to say whether the mixture in the smoke arises from contributions suddenly cooled from different parts of the arc which are at different temperatures, or whether it is due to the reactions (4) and (5) becoming arrested by the cooling before reversion to cupric oxide is completed. In either case, the majority of the smoke particles in the sample examined must have been formed at temperatures in the neighbourhood of 1000° C.

Gold.—Gold, the remaining metal of the copper group, was dispersed from thick foil rolled into the form of rods and used as electrodes in the arc. The lines in the spectrum from the deposited smoke were all due to metallic gold.

Iron.—The smoke from iron electrodes consisted of a mixture of iron oxides. All the lines in the spectrum could be accounted for on the supposition that the deposit consisted of a mixture of paramagnetic ferric oxide and ferro-ferric oxide. The latter (magnetite) is cubic and the former is rhombohedral, isomorphous with α Al_2O_3 . Like Al_2O_3 , ferric oxide is polymorphous. Magnetite on oxidation to ferric oxide at comparatively low temperatures is converted into the ferromagnetic iron oxide γ Fe_2O_3 , which is reported to

* If the partial pressure were half the normal, *i.e.*, 77 mm., the temperatures change from 1026° C. and 1135° C. to 989° C. and 1161° C. respectively.

give an X-ray spectrum identical with that from magnetite itself, the spacings agreeing with one-tenth of one per cent.⁽⁹⁾.

Ferromagnetite ferric oxide γ Fe_2O_3 is permanently transformed into the commoner paramagnetic α Fe_2O_3 at a higher temperature, the exact value of which depends largely on its mode of preparation⁽¹⁰⁾. Thus if the oxidation of iron to ferric oxide in the dispersal process occurs with Fe_3O_4 as an intermediate product, it is possible that the smoke contains a proportion of γ Fe_2O_3 , but this apparently cannot be decided from X-ray data alone.

A test with potassium ferricyanide failed to confirm the presence of ferrous iron in the precipitated smoke. Hence the smoke must consist of a mixture of α Fe_2O_3 and γ Fe_2O_3 .

Since magnetite and the ferromagnetic iron oxide have substantially the same susceptibility—some 10,000 times that of α Fe_2O_3 —the magnetic properties of the smoke and of the deposit from it will be practically the same as if the smoke consisted of a mixture of magnetite Fe_3O_4 and the non-magnetic ferric oxide.

The occurrence of γ Fe_2O_3 is therefore of interest in connexion with a magneto-optical effect with fumes from an iron arc, described a few years ago by Elihu Thomson⁽¹¹⁾. The smoke particles from an iron arc tend to form thread-like complexes on aggregation. Normally, owing to Brownian movements, the complexes in the smoke will be oriented at random, but in the presence of a magnetic field the magnetic aggregates will tend to lie along the lines of force, thereby producing a vectorial or anisotropic property in the smoke. It is to be expected that such a property will be revealed by the optical behaviour of the system.

Thomson illuminated the smoke by a beam of sunlight and arranged to produce a magnetic field in it with the lines of force perpendicular to the incident beam. When viewed in a direction making a small angle with the beam, the smoke becomes luminous when the field is on and invisible when the field is off. The light diffracted from the luminous cloud in a plane perpendicular to the lines of force is partially polarized. On the assumption that the particles were magnetic, Thomson attributed the effect to the lining up of the chains of particles under the influence of the field. The increased diffraction from the oriented particles accounts for the extra visibility when the field is on. On removal of the magnetic field, Brownian movement obviously destroys the structure and the visibility of the smoke diminishes. The results of the X-ray analysis remove the need for the assumption. They further explain another effect observed

by Thomson. This, perhaps, is best described by a quotation from the letter to 'Nature':—

"Moreover, the very curious fact was discovered by me, that the fumes from the iron arc were composite so far as analysis by the polarizing prism was concerned. The bluish-coloured smoke arising gave but little effect, but there was with it a yellowish-grey fume, which was highly luminous in one position of viewing by the prism, and invisible when the prism was at right angles to that position. This indicates complete polarization when the field is on for the light diffused from the particles in the yellowish-grey fumes. This is an extraordinary effect for which no explanation suggests itself."

We have seen that the fumes are composite so far as analysis by X-rays is concerned. They contain the magnetic γ Fe_2O_3 and the non-magnetic α Fe_2O_3 . Evidently the blue-coloured fume, which presumably is given off from the core of the arc, consists mainly of paramagnetic ferric oxide particles, whilst the yellowish-grey fume consists of the ferromagnetic oxide. The difference in colour, of course, depends upon the size of the particles, the α Fe_2O_3 particles being the smaller. The difference in size of the particles of the two substances should be manifest on the powder photograph, for the smaller α Fe_2O_3 particles would give lines which were more broad and diffuse than those due to the magnetic oxide. This actually appears to be the case, but without accurate measurement the point cannot be fully decided. The higher temperature of the central portion of the arc is conducive to greater chemical activity and to a greater concentration of dispersed matter. By von Wiemarn's law of corresponding states, it is to be expected that the resulting degree of dispersion of the paramagnetic particles will be greater and therefore the average size of the particles less than in the fume from the outer and cooler portions of the arc. The separation of the fume as revealed by its colour and the magneto-optical effects suggests that the γ oxide formed results from oxidation of the iron in the cooler portions of the arc. We should obtain a lower limit to the temperatures at which the smoke particles are formed if we assumed that the γ Fe_2O_3 results from the intermediate formation of Fe_3O_4 . Welo and Baudisch⁽⁹⁾ obtained γ Fe_2O_3 by heating Fe_3O_4 to 220° C. in air. Sosman and Hostetter⁽¹²⁾ found that magnetite begins to oxidize at an observable rate at 300° C., but it appears⁽¹⁰⁾ that different varieties of magnetite exhibit great differences in their resistance to oxidation, and therefore in the temperatures necessary to

ensure completion of the reaction. It seems as difficult at present to fix a temperature of formation of $\gamma \text{Fe}_2\text{O}_3$ as it is to give a temperature for its transformation into $\alpha \text{Fe}_2\text{O}_3$.

According to O. Wiener⁽¹³⁾, if a substance consists of aggregates of parallel rods, it will show double refraction. Virtually such aggregates behave as uniaxial crystals. This seems the type of structure produced in an iron smoke by a magnetic field. Hence we may expect an iron smoke to show double refraction. Tieri⁽¹⁴⁾ finds that it gives a positive birefringence. He also noted that a copper smoke in a sufficiently intense field was doubly refractive. This is undoubtedly due to the paramagnetism of cupric oxide⁽¹⁵⁾.

Platinum.—The electrodes of the platinum arc consisted of platinum-foil rolled into the form of rods. Like the silver arc between foil electrodes, the platinum arc was difficult to maintain and probably ran at a temperature lower than would have obtained had the electrodes been solid rods of the metal. Only lines due to metallic platinum were found on the film. They were diffuse, as if the particles were very fine. The result accords with the orthodox view that platinum produces a metallic smoke. According to Roberts⁽²⁴⁾, however, a clean platinum wire when heated produced nuclei (particles) only in the presence of oxygen, and not in its absence. He attributed this to the intermediate formation of an oxide and adduces other experimental evidence in support of the hypothesis. Platinum would then behave like silver, which seems plausible. The subject might repay further investigation.

Lead.—Lead gave only lines due to the rhombic yellow monoxide. This modification is formed when the fused oxide is cooled. It is unstable and turns into the red modification at room temperatures, the transformation being accelerated apparently by rubbing⁽¹⁶⁾. It is probably the modification which is formed from lead carbonate by heating at 600°C . The X-ray spectrum, which was taken immediately after the smoke had been precipitated, showed no traces of the tetragonal red monoxide.

Arsenic and Antimony.—The smokes from these metals consisted of the sesquioxides. These are said to be isodimorphous. Both exist in a cubic form. Sb_2O_3 possesses an orthorhombic modification (valentinite) and As_2O_3 has an orthorhombic (Dana⁽¹⁷⁾) or a monoclinic (pseudorhombic) form⁽¹⁸⁾. Both forms of As_2O_3 are obtained by sublimation. According to Dana, the prismatic form is only

obtained at a temperature above 200° C. and the cubic form at one much lower. Valentinite is the high temperature form of Sb_2O_3 . The structures of the cubic forms have been given by Bozorih⁽¹⁹⁾, but no data about the other modifications seem available. The cubic form was obtained with the smoke from arsenic, but not with the smoke from antimony. The latter appeared to be orthorhombic. The number of lines obtained in the spectrum, however, was insufficient to give reliable constants by the method of successive approximations, so the observations were reduced by assuming Dana's values for the axial ratios $a : b : c = 3.587 : 1 : 2.536$. Apparently the disperse phase in the case of arsenic was formed at a temperature not greater than 200° C. This seems plausible. Comparatively large pieces of arsenic were used as electrodes in the arc and the smoke was found to be very readily produced. Contrary to what occurred with antimony, the arsenic electrodes hardly got warm.

The supposition that dispersal occurred at a relatively low temperature in the case of arsenic receives some support from the colour of the precipitated smoke, which was grey and not the usual white associated with arsenious oxide. The colour probably arises from traces of metallic arsenic, although the quantity present was insufficient to produce a recognizable spectrum.

Aluminium.—The smoke from aluminium consists of alumina. Al_2O_3 crystallizes in three forms known as α , β , and γ corundum. The first is rhombohedral (ruby type), isomorphous with the crystals of Fe_2O_3 and Cr_2O_3 found in the smokes from iron and chromium; the second is hexagonal, and the third is said to possess the same structure as ferromagnetic Fe_2O_3 , so is presumably cubic. The spectrum of the precipitated smoke from aluminium electrodes showed no lines which could be attributed to the commoner rhombohedral form. With the exception of six weak lines, the spectrum agreed with that to be expected from β corundum. The six weak lines were not identified with certainty. They are not due to metallic aluminium, and, since even the commercial metal is now 98-99 per cent. pure, it seems unlikely that they are due to impurities in the aluminium. Their positions agreed tolerably well with possible reflexions from a cubic lattice with $a = 6.53$ Å. The smoke therefore consists mainly of β corundum, a hexagonal crystal, with possibly a small admixture of the γ type.

Silica.—This substance was prepared by the combustion of carborundum SiC in the crater of a carbon arc. The smoke

gave a translucent white deposit which on analysis failed to give a characteristic spectrum with either $\text{CuK}\alpha$ or Fe radiation. A close examination of the film which had received the longest exposure revealed a few faint lines which normally would almost certainly have passed unobserved. These, however, were all found to agree with reflexions from carborundum I. No trace whatever was found of the spectra from either α or β quartz, α or β tridymite, or β cristobalite. The material is, therefore, amorphous silica containing traces of carborundum as impurity. According to the phase diagram of Fenner⁽²⁰⁾, the amorphous form of silica—silica glass—is the modification which is stable at temperatures greater than 1625°C . It seems reasonable to infer that the silica smoke was produced at a very high temperature. It is difficult to disperse and requires a high current density, but once dispersal has commenced smoke production is not so difficult to maintain. The retention of the phase as the smoke cools is materially assisted by the sluggishness exhibited by silica in its changes from one state to another.

Bismuth.—The bismuth arc gave a smoke of Bi_2O_3 . This is said to be polymorphous; crystals attributed to the cubic system and to the orthorhombic have been described (Groth), but no X-ray data about the substance seems available. The spectrum obtained from the smoke with $\text{CuK}\alpha$ radiation consisted of about 53 lines which could all be accounted for as reflexions from a tetragonal lattice. As it is difficult to be certain from a powder photograph alone that the lines are not due to a mixture of two types of crystal, the lattice constants given in the table are offered as a possible unit cell.

Tungsten.—Tungsten was dispersed by fusing a wire of the metal in air with a heavy current. About 120 lines were measured on the film, which was taken with $\text{CuK}\alpha$ radiation. The absence of data upon a single crystal of the trioxide makes it impossible to check the identification of the planes responsible for the lines. Hence the constants of the orthorhombic lattice given are those of a possible unit cell. The ratios of the constants, $a : b : c = 0.7000 : 1 : 0.3988$ happen to agree with the axial ratios given by Nordenskiöld for tungstite and quoted by Dana⁽¹⁵⁾, viz. $0.7002 : 1 : 0.3991$.

Manganese.—According to Kohlschütter and Tüscher, the precipitated smoke from manganese consists of a mixture of manganese sesquioxide Mn_2O_3 and manganese dioxide MnO_2 .

The sample examined by X-rays, although prepared by the same method, was found to consist of the red manganese oxide Mn_3O_4 . As Mn_3O_4 is the most stable of the oxides and is formed when either Mn_2O_3 or MnO_2 is strongly heated, the discrepancy may be merely a temperature effect. All the lines observed were accounted for and no trace was found of lines attributable to MnO_2 or Mn_2O_3 .

Tin.—The analysis of the precipitated smoke from tin electrodes was the least satisfactory of all attempted. The smoke, which is probably wholly stannic oxide, is produced at a relatively low temperature, probably not much higher than the melting-point of tin 232°C .; for as soon as the electrode ends soften they drop off under their own weight and extinguish the arc. This is conducive to the formation of unstable modifications of SnO_2 if such exist. The commonest form of SnO_2 is cassiterite, a tetragonal crystal similar to rutile (TiO_2), but two other modifications have been reported—a rhombic, analogous to brookite (TiO_2), and a pseudohexagonal similar to tridymite (SiO_2). The powder photograph showed that the precipitate did not consist of cassiterite, although spacings were present which agreed closely with all those given by cassiterite. The material may therefore consist of the common tetragonal form of SnO_2 with possibly another modification present as well. This is the result tabulated but pending further investigation it is given with great diffidence. It shows, however, that the interatomic distances in the crystalline smoke particles are closely similar to those in cassiterite, so the respective densities cannot differ greatly.

The Densities of the Particles.

It will be seen from the results in Table I. that the measured constants closely agree with the comparison data. The variation is no greater than that observed amongst the values published by different observers for the same crystal. The size of the unit cell in constituent particles of any smoke is therefore identical with that in a macroscopic crystal of the same material. Moreover, the relative distribution of intensity amongst the spectral lines for any given substance was found to be the same for both the smoke particles and for the crystallized material wherever published data were available for reference. Hence the atoms occupy similar positions within the unit cells in both cases. It follows that the homogeneous particles in the precipitated

smokes have the normal density of the same material when it occurs as a crystal.

The results also show that the crystalline smoke particles are usually formed at a high temperature, probably close to the pole pieces of the arc, and that they cool rapidly as they leave it. The particular crystalline structure acquired on formation is thereby conserved, with the result that the dispersoid from polymorphous substances usually possesses the modification which is stable at high temperatures.

The results as a whole suggest that the formation of the primary particles of a smoke takes place suddenly during the condensation process and under equilibrium conditions both internally and externally with respect to the particle. The external conditions determine the chemical nature of the particle and are controlled by the thermodynamical equations appropriate to the chemical reactions occurring; the internal equilibrium determines the molecular structure of the particle and is, presumably, governed by the laws of lattice dynamics.

Although X-rays reveal the internal structure, they give no information about the shape of the particles. In almost all cases the particles are of ultramicroscopic size and therefore give diffraction disks and not images when examined optically. In the past the ultramicroscopic particles have been considered spherical—mainly, perhaps, as a matter of convenience. We expect liquid particles like oil drops to be spherical owing to the action of surface tension, but as many of our oxides from their known chemical properties, *e. g.*, Ag_2O , CuO , can never have been liquid, we cannot suggest in these cases that the particles are solid spheres resulting from sudden chilling after fusion.

From a crystallographic standpoint there is no reason why the ultramicroscopic particles should not be faceted and possess external forms precisely like macroscopic crystals grown under similar conditions. The photomicrograph, fig. 1 of the paper of Paterson and Whytlaw-Gray⁽⁶⁾ shows that the larger particles in the deposit from a magnesium oxide smoke are faceted. Kohlschütter and Tüscher found that the particles in the smoke from arsenic were microscopic crystals. By regulating the rate of smoke production they obtained minute crystals from sparse antimony oxide smokes, whilst from denser smokes the particles appeared smaller and showed no recognizable form. A change in size only, in the direction demanded by von Weimarn's law of corresponding states, seems adequate to explain the appearance of the precipitate in the latter case.

The manner of aggregation of the particles provides evidence bearing on this point. It is well established that after formation the primary particles in a smoke disappear by a process of aggregation. If this takes place along a concentration gradient or in an electric field the resulting aggregates are thread-like. This peculiarity has long been known, and was observed in greater or less degree with all the substances examined. From their behaviour in a current of air, when one end is fixed on, say, an electrode of the electric field, it is clear that the filaments can withstand tension, although they are probably never as strong as a spider thread. In the case of cadmium oxide, where they are obtained with comparative ease, it has been shown that the individual particles in the chains are oriented in the direction of a crystallographic axis⁽²¹⁾. It seems probable that this occurs in all cases. Taking into consideration that in the chain-like filaments we are dealing with the arrangements of the individual particles, irrespective of size, and that the strength of the filament must be determined by the strength of its weakest link, this behaviour seems inexplicable if we assume that the particles are spherical, each touching its neighbour at a mathematical point. If, however, the particles have the external forms of crystals, we get surfaces in contact; in the case of cadmium oxide, like faces (mostly dodecahedron faces) are in contact, and the growth of these structures seems inevitable.

Until, therefore, we obtain unimpeachable evidence to the contrary, we may assert that the primary particles are bounded by plane faces. The particles in the smokes examined, with the sole exception of silica, are therefore crystals of the dispersoid, similar in internal structure and external appearance with the specimens exhibited by crystallographers. They differ mainly in the matter of size.

In conclusion, I wish to thank Mr. C. H. Gregory for his valuable assistance in obtaining powder photographs, and Prof. W. L. Bragg for the interest he has taken in the work.

SUMMARY.

The precipitated smokes dispersed by an arc from about twenty common metals have been examined by the powder method of X-ray analysis and found to be crystalline. The particles in a smoke of SiO_2 dispersed from carborundum were amorphous and consisted of silica glass. Platinum and gold gave metallic smokes.

Smokes which consist of oxides which are polymorphous, usually give the modification which is stable at high temperatures. The smokes from copper and iron give mixed oxides. This seems due to dissociation in the first case and to low temperature oxidation in the second. These results indicate that the formation of the smoke particles is completed at a high temperature and in the immediate neighbourhood of the hot electrodes.

The results for iron are shown to complete the explanation offered by Elihu Thomson of a magneto-optical effect observed with the fume from an iron arc.

The densities of the crystalline particles in the smokes are normal. The abnormally low values found by previous investigators, using other methods, are attributed to the mode of aggregation of the particles.

References.

- (1) Kohlschütter and Tüscher, *Zeit. f. Electrochemie*, xxvii. p. 225 (1921).
- (2) Gerlach, 'Materie Elektrizität Energie,' p. 53 (T. Steinkopff, 1923).
- (3) Bär, *Ann. d. Phys.* lxvii. p. 157 (1922).
- (4) Sexl, *Zeit. f. Phys.* xvi. p. 34 (1923).
- (5) Patterson and Whytlaw-Gray, *Proc. Roy. Soc. A*, cxiii. p. 302 (1926).
- (6) Broch, *Zeit. phys. Chemie*, cxxvii. p. 446 (1927).
- (7) Von Wartenberg, *Zeit. f. Electrochemie*, xix. p. 487 (1913).
- (8) Smyth and Roberts, *J. A. C. S.* xlii. p. 2582 (1926); xliii. p. 1061 (1921).
- (9) Welo and Baudisch, *Phil. Mag.* l. p. 399 (1925).
- (10) Herroun and Wilson, *Proc. Phys. Soc.* xli. p. 100 (1928).
- (11) Elihu Thomson, 'Nature,' cvii. p. 520 (1921).
- (12) Sosman and Hostetter, *J. A. C. S.* xxxviii. p. 807 (1916).
- (13) Wiener, *Abh. d. Sachs. Ges. d. Wiss.* xxxii. p. 6 (1912).
- (14) Tieri, 'Nature,' cvii. p. 778 (1921).
- (15) Birch, *J. Phys. Rad.* (6) ix. p. 137 (1928).
- (16) Ruer, *Zeit. f. anorg. Chem.* l. p. 265.
- (17) Dana, 'Descriptive Mineralogy' (1892).
- (18) Groth, *Chem. Kryst.* i. (1906).
- (19) Bozorth, *J. A. C. S.* xlv. p. 1621 (1923).
- (20) Fenner, *Am. Jour. Sc.* xxxvi. p. 331 (1913).
- (21) Walmsley, *Proc. Phys. Soc.* xl. p. 7 (1927).
- (22) Gottfried, *Zeit. f. Kryst.* lxvi. p. 393 (1928).
- (23) Aminoff, *Zeit. f. Kryst.* lxiv. p. 475 (1926).
- (24) Roberts, *Phil. Mag.* (6) xxv. p. 270 (1913).
- (25) Kaye and Laby, 'Tables of Physical and Chemical Constants,' (1916).
- (26) Halla and Pawlek, *Zeit. f. phys. Chem.* cxxviii. p. 49 (1927).

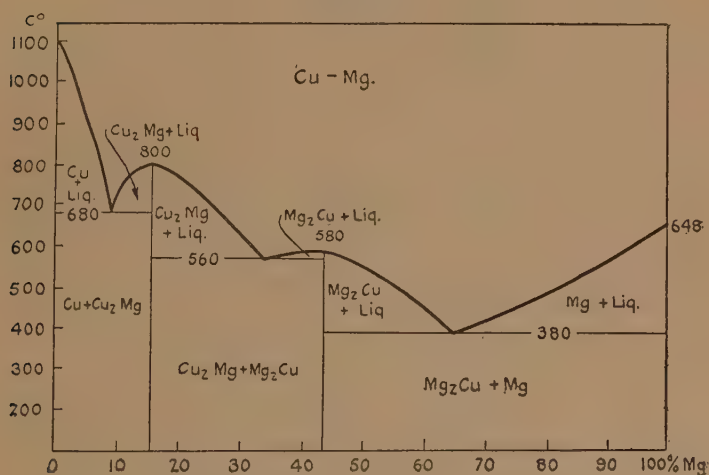
The Physical Laboratories,
The University, Manchester.

CXXVI. *An X-Ray Investigation of the Copper-Magnesium Alloys.* By GEOFFREY GRIME, M.Sc., and W. MORRIS-JONES, M.A., M.Sc. (Department of Physics, University College, Swansea) *.

INTRODUCTION.

THE most thorough investigation of the copper-magnesium system of alloys is that of Sahmen †. His work, published in 1908, led him to the equilibrium diagram given in fig. 1. This diagram is taken as the basis of comparison in the present investigation.

Fig. 1.



Sahmen's equilibrium diagram.

The diagram is a simple one, and consists of three sections, each of which may be considered as a separate system. The systems are Cu—Cu₂Mg, Cu₂Mg—Mg₂Cu, and Mg₂Cu—Mg. Each of the sections shows the behaviour of two constituents soluble in each other in all proportions when hot, but insoluble when cold. The system has, therefore, two maxima at compositions represented by the formulæ Cu₂Mg and Mg₂Cu, and three minima at intermediate eutectic compositions. The metallurgical data all point to the

* Communicated by W. Morris-Jones, Senior Lecturer in Physics, University College, Swansea.

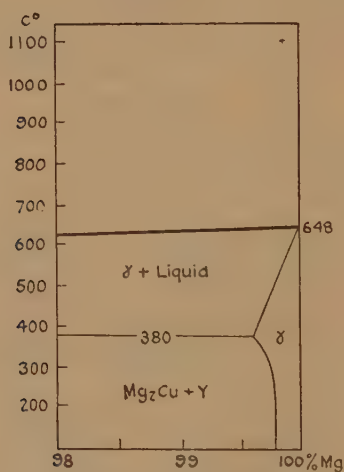
† *Zeit. Anorg. Chem.* lvii. pp. 1-33 (1908).

existence of intermetallic compounds at the compositions represented by the maxima.

An earlier work by Boudouard * supplies the only evidence against the form of the curve. He found an additional maximum corresponding with a composition CuMg, but was unable to isolate the assumed compound. Neither diagram (Sahmen's nor Boudouard's) shows any regions of solid solutions—both are ideal examples of their type.

Hansen †, by a microphotographic investigation, carried out in 1924, on the magnesium-rich alloys, claimed to have proved that magnesium can hold copper in solution at

Fig. 2.



Mg end of diagram according to Hansen.

ordinary temperatures to the extent of something approaching 0.2 per cent. This, if confirmed, would result in the modification of the magnesium end of the diagram to the form given in fig. 2. Jenkin, however, in the discussion ‡ on the above-mentioned paper, disputed the accuracy of these inferences, and put the solubility of copper as very much less. From examination of the microstructure of alloys prepared and examined by him, he inferred that the solubility of copper in magnesium is less than 0.04 per cent.

* *Compt. Rend.* cxxxv. pp. 794-796 (1902); cxxxvi. pp. 1327-1329 (1903).

† *Journal of Institute of Metals*, p. 93 (1927).

‡ *Loc. cit.*

The present investigation was undertaken as it was thought that an X-ray study of the system, while of interest as a problem in crystal analysis, would yield evidence of the formation of solid solutions undetected by metallurgical investigation; and would, in particular, throw light on the unsettled problem of the solubility of copper in magnesium. The lattice of such solid solutions would differ slightly in dimensions, but not in crystallographic system, from those of the pure solvent. A series of eight alloys, of composition ranging from pure copper to magnesium, were therefore prepared and their crystal structures examined by the X-ray powder method.

Preparation of Alloys.

The alloys, containing from 0 per cent. to 47 per cent. magnesium, were prepared by the method adopted by Boudouard*.

The materials used were electrolytic copper and magnesium of high purity. The copper was melted under a layer of charcoal in a salamander pot, in which scrap magnesium had previously been melted to take up any active material from the walls, and to form a protective lining. When molten, the metal was stirred with a carbon rod, to get rid of oxygen, and then most of the charcoal layer was scraped off. Sodium chloride, to form a molten layer about half an inch thick, was placed in the pot. When the metal and flux were completely fluid once more, the magnesium was introduced in large pieces and held beneath the surface of the copper with a tongs until liquid. After the first piece had been introduced, the temperature of the furnace was allowed to decrease, for, as may be seen from the equilibrium diagram, the melting-point of the alloy drops very steeply with increasing magnesium content. Lowering the temperature prevents loss of magnesium by oxidation, which is very likely to take place if the furnace is too hot. When the calculated weight of magnesium, with a few grams over to allow for oxidation, had been introduced, the alloy was stirred, left in the furnace for a few minutes, and then withdrawn and allowed to cool in the pot. A wind furnace was used, and ingots of 200-300 grms. were prepared each time.

In preparing alloys having a higher magnesium content the method of Cook and Jones† was employed.

* *Loc. cit.*

† *Journal of Institute of Metals*, pp. 36, 157 (1926).

The alloys were made in an iron crucible, in a small gas furnace capable of raising the temperature of a small melt to about 800°C . The copper was introduced in the form of a 64-per-cent. copper-magnesium alloy, which was melted up with the calculated amount of magnesium under a flux of one part of magnesium chloride to one part of potassium chloride.

This flux melts between $400\text{--}500^{\circ}\text{C}$., which is lower than the melting-point of any of the alloys. It therefore covers the whole charge with a protective layer of flux while melting takes place. Sodium chloride cannot be used in this method as its melting-point is considerably above that of the alloys to be prepared.

The iron pot was first heated up and scrap magnesium melted in it, as before, to form a coating. The flux, which is very deliquescent, was prepared fresh each time by heating up the constituents together on an iron ladle until all the water had been driven off and the flux had fused. It was then poured on to a cold iron slab and, when cold, was powdered up ready for use. The charge, consisting of the calculated weights of magnesium and the alloy, broken into small pieces, was introduced into the crucible and covered with a layer of flux—about 3–4 per cent. by weight of the charge—this being the proportion found most suitable by Cook and Jones*. The crucible was covered by a lid and raised to a temperature sufficient to melt the magnesium, and kept there until, on stirring, the liquid felt perfectly uniform. The crucible was then withdrawn from the furnace and allowed to cool.

For those alloys whose density was required, the process of double melting was resorted to, in order that the ingots might be sound. The alloy was allowed to solidify, and was then re-melted quickly and allowed to cool to room temperature. This process gets rid of the peculiar radially-disposed blow-holes, which are present in the once-cooled copper-magnesium alloys.

The composition of the alloys was determined by the estimation of the copper-content, the magnesium being estimated by difference, as this involves less error than determining it directly.

The copper was estimated by an electrolytic method, using a rotating cathode. The platinum cage, forming the cathode, was rotated by a small electric motor. A second stationary electrode of platinum disposed co-axially about the cathode

* *Loc. cit.*

formed the positive pole. The solution, containing 1 gram of the alloy dissolved up in nitric acid, generally took about an hour and a half to be electrolysed. From the weights of alloy taken, and the copper deposited on the cathode, a simple calculation gave the percentage composition of the sample. The densities of the alloys were determined by the suspension method, using small polished specimens with acetone as the immersion fluid. The composition and densities of the alloys are given in Table I.

Method of X-Ray Analysis.

The well-known powder method of Hull was used in the investigation. In this method a disordered mass of very fine crystals is placed along the axis of a cylindrical camera, and when irradiated with a narrow beam of X-rays gives rise to a series of lines on a strip of photographic film disposed around the circumference of the cylinder.

The information furnished by the photograph consists of interplanar distances in the crystal structures, together with the intensities of the lines produced by the set of planes having these interplanar distances.

Details of the apparatus used in the present investigation have been given in a previous paper*, and need not be described here.

The procedure employed in preparing the powder was the following.

The material was broken up into small pieces and ground down as fine as possible in a small agate mortar. It was found that the alloys of high magnesium-content attacked the mortar during grinding, leaving a thin skin of copper colour on the surface—probably due to the combination of the active magnesium with the material of the mortar, when heated by grinding. This was remedied by grinding under acetone, which kept the powder cool. The finest particles were then separated by a process of decantation. The powder was shaken round with acetone in a beaker, and the top portion, containing the lightest particles, decanted off on to a filter-paper and there collected.

Alloys which, owing to their ductile nature, could not be broken up by grinding were rubbed off with fine emery-cloth, and the process of decantation carried out on the powder so obtained.

A cylindrical glass fibre was situated along the axis of the camera. The powder was painted on this fibre with an

* Morris-Jones & Evans, *Phil. Mag.* iv. (December 1927).

organic adhesive to the thickness of $1/10$ mm., resulting in a powder-coated rod of diameter 0.70 mm. Its diameter was measured each time with a travelling microscope to ensure that the variation should not exceed 0.05 mm. An exposure of two to three hours was generally sufficient for a good photograph. The developed photograph was mounted on the table of a travelling microscope, and the distances of the lines from the central zero position were measured. A correction has to be applied for the diameter of the cylindrical glass fibre. This is best done by standardising the camera with the lines from a lattice of accurately known dimensions. Such a standardisation will rectify all permanent errors of the camera, such as faulty centring of the specimen and imperfect shape of the camera.

Sodium chloride, which gives an excellent pattern of evenly-spaced intense lines, was used for the standardisation. Its lattice, which is accurately known, is cubic with a base $a_0 = 5.628$ Å.U.

From the corrected distances on the film the diffracting angles θ_1, θ_2 etc. were calculated, and from these angles the interplanar spacings d/n were found, using the formula

$$\frac{\lambda}{2} = \frac{d}{n} \sin \theta.$$

These spacings, together with the intensity of the lines, constitute the information available from powder photographs, and the crystal structure has, if possible, to be deduced from it.

For the accurate determination of the dimensions of the crystal lattice, only those lines between 40 and 60 mm. from the zero position were used. This range was chosen as furnishing the most accurate measurements, from the following considerations:—

(a) It was found from experience that up to 80 mm. from the centre of the films the maximum error in marking the films amounted to 0.1 mm. It is therefore of advantage to use those lines in this range which are furthest from zero, since the proportional error in measurement is then least.

(b) The lines diffracted at large angles come off the broad surface of the specimens nearest the slit, and are diffuse and difficult to mark accurately.

The region 40 to 60 mm. from zero offers the best compromise between large deviation and fineness of line, and has been used for the accurate determination of the unit

cell whenever more than two lines were present in that region.

Another factor in the accuracy of measurement is the variation of absorbing power in the different substances investigated. Assuming that the diameter of the specimen is the same in each case, as was actually ensured by measurement, then the lower the absorbing power of the alloy, the further in towards zero are the lines, and the correction curve would only hold good if both powdered specimens (after being painted on) possessed the same absorbing power. In practice, the effect was reduced to a minimum by powdering the substance very finely to ensure a high surface-density. Under these circumstances, and with the soft copper radiation used, the diffraction could be considered as taking place from practically the surface of the cylinder. Observing these precautions, and using lines between 40 and 60 mm. from the zero position, the accuracy may be estimated as within $1/6$ of 1 per cent.

RESULTS.

The chemical composition of the eight alloys, as determined by analysis, are given in Table I. Two photographs were taken of each alloy; the measurements given in the appropriate tables are the mean of the results from the two films. The second exposure was taken to prevent the possibility of error due to the positioning of the film.

The results of the X-ray investigation of the crystal structures confirm, in the main, the equilibrium diagram of Sahmen, *i. e.*, that it consists of three sections and shows maxima at the compositions corresponding with the formulæ Cu_2Mg and Mg_2Cu . No evidence of Boudouard's third compound CuMg was obtained. In addition, the X-ray investigation revealed two new regions of solid solution. These were:—

(a) A solution of magnesium in copper up to approximately 3 per cent. magnesium.

(b) A region of solid solution extending on both sides of the Cu_2Mg composition.

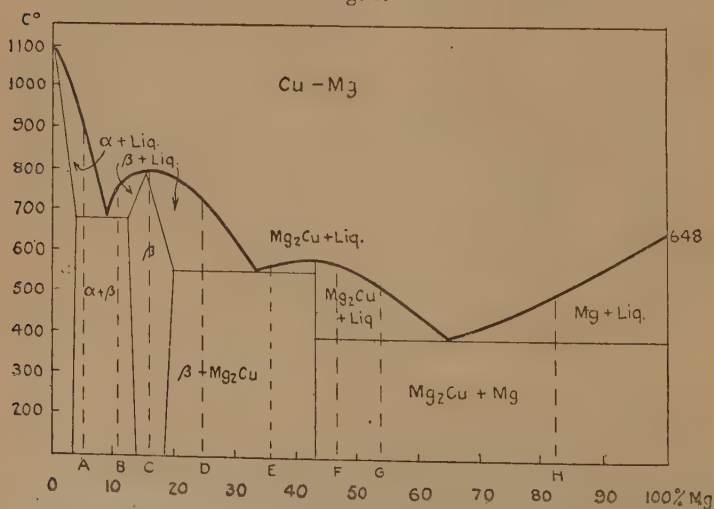
In every other particular the original diagram was corroborated. No trace of solid solution could be detected at the magnesium end. Variation in the position of the lines, due to the magnesium lattice, was particularly small.

An examination of column 5 of Table I. shows that the dimensions of the magnesium lattices determined from alloys G and H differ from those of the pure metal by only one part

TABLE I.

Alloy.	Composition.	Density.	Type of lattice.	Length of base (in Å.U.).
	per cent. Mg.			
Copper	0	8.94	Face-centred cubic.	$a_0 = 3.610$
A.....	5	8.61	Face-centred cubic.	$a_0 = 3.634$
B.....	11	6.64	Mixture of two face-centred cubic systems.	$\begin{cases} a_0' = 3.630 \\ a_0'' = 7.003 \end{cases}$
C.....	16	5.72	Face-centred cubic.	$a_0 = 7.034$
D.....	25	5.02	Face-centred cubic and hexagonal.	$\begin{cases} a_0' = 7.059 \\ a_0'' = 5.288 \end{cases}$
E.....	36	3.90	Face-centred cubic and hexagonal.	$\begin{cases} a_0' = 7.066 \\ a_0'' = 5.276 \end{cases}$
F.....	47	3.18	Hexagonal.	$a_0 = 5.281$
G.....	54	3.05	Mixture of two hexagonal systems.	$\begin{cases} a_0' = 5.280 \\ a_0'' = 3.205 \end{cases}$
H.....	82	2.22	Mixture of two hexagonal systems.	$\begin{cases} a_0' = 5.280 \\ a_0'' = 3.205 \end{cases}$
Magnesium...	100	1.74	Hexagonal close packed.	$a_0 = 3.206$

Fig. 3.



Equilibrium diagram as modified by X-ray investigation of the system.
Dotted verticals are erected at compositions investigated.

in 3200. The solubility of copper in magnesium is therefore exceedingly small—probably the order suggested by Jenkin.

The equilibrium diagram modified by the results of the X-ray investigation is given in fig. 3. The dotted verticals on the diagram show the compositions at which photographs were taken.

The α Phase.

The α phase (see fig. 3) was investigated with the aid of powder photographs of copper, and of alloys A and B. The data are given in Tables I., II., III., and IV.

TABLE II.—Copper.
(Face-centred cubic.)

Radiation.	$h\ k\ l$.	Intensity.	d/n observed.	d/n calculated.
K_{β}	111	W.	2.082	2.084
K_{α}	111	St.	2.084	2.084
K_{α}	100	St.	1.804	1.805
K_{α}	110	St.	1.275	1.276
K_{α}	131	St.	1.089	1.088
K_{α}	111 (2)	M.	1.042	1.042

NOTE.—In Tables II.–XI. the first column states the quality of the copper radiation; the second, the indices of the plane spacings referred to rectangular or hexagonal axes according to the type of structure found; the third, the intensities of the lines on the photograph; and the fourth gives the plane spacings obtained from measurements on the films. The fifth column gives the calculated plane spacings for the respective lattices obtained.

The intensities of the lines are denoted by the symbols St.=strong; M.=medium; W.=weak; V.W.=very weak.

TABLE III.—Alloy A (5 per cent. Mg).
(Face-centred cubic.)

Radiation.	$h\ k\ l$.	Intensity.	d/n observed.	d/n calculated.
* K_{β}	111	V.W.	4.186	4.043
* K_{α}	111	V.W.	4.029	4.043
K_{β}	111	M.	2.089	2.089
K_{α}	111	St.	2.098	2.098
L_{α} (tungsten) .	100 (2)	W.	1.820	1.817
K_{α}	100 (2)	St.	1.821	1.817
K_{α}	110 (2)	St.	1.283	1.284
L_{α} (tungsten) .	131	W.	1.093	1.096
K_{α}	131	St.	1.094	1.095

NOTE.—Lines of β phase are marked with an asterisk (*).

The copper lattice, whose dimensions have been determined frequently but not conclusively, was found to have the known face-centred structure with a base $a_0 = 3.610$ Å.U. The copper used was high-grade electrolytic metal of 99.88 per cent. purity, powdered by friction with emery-cloth and tested, as described in a previous section. The phase in which copper is the solvent has the same face-centred

TABLE IV.—Alloy B (11 per cent. Mg).
(Mixture of two face-centred cubic systems.)

Radiation.	hkl .	Intensity.	d/n observed.	d/n calculated.
* $K\alpha$	111.	M.	4.047	4.043
* $K\alpha$	110 (2)	W.	2.481	2.476
* $K\alpha$	131	St.	2.112	2.112
* $K\alpha$	111 (2)	St.	2.024	2.022
$K\alpha$	100 (2)	M.	1.817	1.817
* $K\alpha$	100 (4)	M.	1.752	1.751
* $K\alpha$	331	M.	1.607	1.607
* $K\alpha$	112 (2)	W.	1.429	1.429
* $K\alpha$	151	St.	1.347	1.348
$K\alpha$	110 (2)	M.	1.283	1.285
* $K\alpha$	110 (4)	St.	1.237	1.238
* $K\alpha$	351	M.	1.183	1.184
$K\alpha$	131	M.	1.093	1.096
* $K\alpha$	253	M.	1.067	1.068
* $K\alpha$	131 (2)	M.	1.055	1.056
* $K\alpha$	111 (4)	W.	1.010	1.011
* $K\alpha$	155	W.	.9807	.9806
* $K\alpha$	371	St.	.9125	.9117
* $K\alpha$	100 (8)	M.	.8981	.8754

NOTE.—Lines of β phase are denoted by an asterisk (*).

structure, but the lattice constant increases with increasing magnesium-content to a constant value about .66 per cent. greater than that of pure copper.

Table III., for alloy A, gives the planar spacings due to such a lattice with base $a_0 = 3.634$ Å.U. This expansion of the unit cell is due to the substitution of the magnesium atoms with their larger atomic radii for some of the copper atoms in the copper lattice.

Two of the innermost lines of the β phase were also present on the photograph, very faintly, constituting evidence that copper holds less than 5 per cent. magnesium in solution at room temperature. The faintness of these lines shows that this composition (5 per cent. magnesium) is near to the limit of solution of magnesium in copper.

This limit may be estimated as falling at about 3 per cent. magnesium at room temperature.

TABLE V.—Alloy C (16 per cent. Mg).
(Face-centred cubic of spinelle type.)

Radiation.	<i>h k l</i> .	Intensity.	<i>d/n</i> observed.	<i>d/n</i> calculated.
K_{β}	111	W.	3·872	4·061
K_{α}	111	M.	4·066	4·061
K_{α}	110 (2)	W.	2·492	2·487
K_{β}	131	V.W.	2·115	2·121
K_{β}	111 (2)	V.W.	2·032	2·031
K_{α}	131	St.	2·125	2·121
K_{α}	111 (2)	St.	2·035	2·031
K_{α}	100 (4)	M.	1·761	1·759
K_{α}	331	M.	1·615	1·614
K_{α}	112 (2)	W.	1·434	1·436
K_{α}	151	St.	1·353	1·354
K_{α}	110 (4)	St.	1·243	1·243
K_{α}	351	M.	1·187	1·189
K_{α}	353	M.	1·068	1·072
K_{α}	131 (2)	M.	1·059	1·060
K_{α}	111 (4)	W.	1·015	1·015
K_{α}	155	W.	·9837	·9849
K_{α}	173	St.	·9157	·9157
K_{α}	100 (8)	M.	·9002	·8793

The photograph of B (Table IV.), showing the lines of the α and β phases, confirms the deductions from A. The lattice constant of the α phase from this photograph is $a=3\cdot630$ Å.U., which is in good agreement with the previous result.

The β Phase.

The structure of the β phase, thought by Sahmen to be Cu_2Mg , has been obtained from a study of the photograph yielded by alloys B, C, and D. The data are given in Tables IV., V., and VI. The phase was found to have a

face-centred structure with a lattice constant which varies from 7.003 to 7.059 Å.U.

TABLE VI.—Alloy D (25 per cent. Mg).
(Mixture of face-centred spinelle structure and hexagonal structure.)

Radiation.	hkl .	Intensity.	d/n observed.	d/n calculated.
K_{α}	10.0	V.W.	4.625	4.573
K_{α}	10.1	V.W.	4.413	4.436
* K_{α}	$\left\{ \begin{smallmatrix} 111 \\ 10.2 \end{smallmatrix} \right\}$	W.	4.084	$\left\{ \begin{smallmatrix} 4.076 \\ 4.089 \end{smallmatrix} \right\}$
K_{α}	10.3	V.W.	3.639	3.658
* K_{α}	$\left\{ \begin{smallmatrix} 110 (2) \\ 11.2 \\ 10.6 \end{smallmatrix} \right\}$	V.W.	2.514	$\left\{ \begin{smallmatrix} 2.496 \\ 2.534 \\ 2.536 \end{smallmatrix} \right\}$
K_{α}	11.3	V.W.	2.408	2.423
K_{α}	$\left\{ \begin{smallmatrix} 00.1 (8) \\ 10.7 \end{smallmatrix} \right\}$	M.	2.270	$\left\{ \begin{smallmatrix} 2.286 \\ 2.269 \end{smallmatrix} \right\}$
* L_{α} (tungsten)	$\left\{ \begin{smallmatrix} 131 \\ 11.5 \end{smallmatrix} \right\}$	V.W.	2.126	$\left\{ \begin{smallmatrix} 2.128 \\ 2.141 \end{smallmatrix} \right\}$
* K_{α}	$\left\{ \begin{smallmatrix} 131 \\ 11.5 \end{smallmatrix} \right\}$	St.	2.133	$\left\{ \begin{smallmatrix} 2.128 \\ 2.141 \end{smallmatrix} \right\}$
K_{α}	$\left\{ \begin{smallmatrix} 10.2 (2) \\ 10.8 \\ 00.1 (9) \end{smallmatrix} \right\}$	St.	2.042	$\left\{ \begin{smallmatrix} 2.045 \\ 2.032 \end{smallmatrix} \right\}$
K_{α}	10.9	V.W.	1.860	1.857
* K_{α}	100 (4)	M.	1.751	1.764
* K_{α}	$\left\{ \begin{smallmatrix} 12.4 \\ 331 \end{smallmatrix} \right\}$	M.	1.619	$\left\{ \begin{smallmatrix} 1.616 \\ 1.619 \end{smallmatrix} \right\}$
* K_{α}	151	M.	1.359	1.359
K_{α}	00.1 (4)	W.	1.308	1.306
* K_{α}	110 (4)	M.	1.247	1.247
* K_{α}	351	V.W.	1.193	1.193
K_{α}	00.1 (16)	V.W.	1.141	1.143
K_{α}	20.1 (2)	V.W.	1.134	1.134
* K_{α}	353	W.	1.074	1.076
* K_{α}	131 (2)	V.W.	1.064	1.064
* K_{α}	111 (4)	V.W.	1.018	1.018
* K_{β}	100 (8)	V.W.	.9064	.8824
* K_{α}	173	M.	.0918	.9190
* K_{α}	100 (8)	W.	.8835	.8824

NOTE.—Lines of the β phase are marked with an asterisk (*).

Friauf* has determined, by powder and Laue methods, the structure of a β -phase alloy said to be Cu_2Mg . This had a face-centred lattice with a base $a_0 = 6.99 \text{ \AA.U.}$, and an experimentally determined density of 5.85 requiring eight molecules in the unit cell. As a result of his work he deduced a structure for Cu_2Mg of the spinelle type, the magnesium and copper atoms having the same arrangement as the metallic atoms in that compound. The atoms of magnesium are arranged in the same manner as the carbon atoms in diamond. This leaves four small cubes, each one-eighth of the unit cell in volume, unoccupied by magnesium atoms. The sixteen copper atoms are disposed in these cubes four in each, symmetrically arranged at the mid-points of the semi-diagonals of each cube.

The results of the present investigation, begun in October 1927, corroborate Friauf's work as to the type, but not the dimensions of the structure. Alloy C has a composition within .6 per cent. of that corresponding to Cu_2Mg (Table I.). Reflexions (Table V.) are present in the first order only from planes having all indices odd, indicating that the lattice is a face-centred one. Its dimensions are $a_0 = 7.034 \text{ \AA.U.}$, a difference of nearly 6 per cent., as compared with Friauf's value. Its density of 5.72 requires eight molecules in the unit cell.

The relative intensities of the lines of the powder photograph were calculated for the spinelle structure, making use of the expression given by Wyckoff† based on the assumption that the scattering power of the atom is proportional to the square of the atomic number.

Satisfactory agreement between the calculated and the observed intensities was obtained. Close agreement could not be expected, since the structure is a complicated one and the formula empirical.

In view of the results about to be detailed, it seems likely that the alloy investigated by Friauf did not have the composition Cu_2Mg , although it may have been homogeneous under the microscope. According to Sahmen's diagram, the β phase consists of pure Cu_2Mg only. The results of the present investigation do not confirm this. The lattice constant varies over a range of composition. The limits of the variation were determined from measurements on alloys B and D. A reference to Table I. and to fig. 3 shows that these two alloys fall, on the equilibrium diagram, B between the α and β phases, and D between the β and Mg_2Cu phases.

* J. Am. Chem. Society, xlix, p. 3107 (Dec. 1927).

† 'The Structure of Crystals,' p. 107.

They should each, therefore, show the lines of two components—the photograph of B showing the lines of the α and the lower limits of the β phases, and that of D showing the lines of the higher limit of the β together with those of the Mg_2Cu phase. Such was found to be the case, and the structure limits of the β phase were thus determined. The measurements are given in Tables IV. and VI., and the resulting limits, as previously stated, are 7.003 Å.U. on the high copper-content side, and 7.059 Å.U. on the high magnesium-content side.

Cu_2Mg can, therefore, hold in solution both copper and magnesium, and the β phase must be a solid solution. Since films of both alloys B and D show the lines of two distinct phases, the limits of the solid solution must be between 89 and 75 per cent. copper. The lines of Mg_2Cu from alloy D are comparable in intensity with those of the β phase. Those of the α phase in the photograph from alloy B are very faint.

The limits of the β phase must therefore, on the one hand, be close to the composition of alloy B, and, on the other hand, be far removed from that of alloy D. It may be estimated that the β phase is confined to 2 or 3 per cent. on either side of the Cu_2Mg composition.

Friauf's value of 6.99 Å.U. for the lattice constant of the alloy examined by him is in close agreement with the value 7.003 Å.U. of the lower limit of the β phase. The density 5.85 of his alloy is that corresponding with a composition of 85.5 per cent. copper, according to the experimental density curve. The method of preparation of the alloy was that of melting together the calculated amounts of magnesium and copper in an electric furnace and allowing the melt to cool slowly. Under these conditions slight loss of magnesium is extremely likely to occur. It therefore seems probable that what he investigated was an alloy having a composition just on the lower limit of solution. If this is assumed, his results agree well with those given here, and the lower limit of the β solution is placed at 85.5 per cent. copper.

The lattice constant of alloy C is 7.034 Å.U. and the experimental density 5.72. The theoretical density, treating the alloy as a solid solution, is 5.76. The discrepancy is probably due to slight porosity of the material.

It is of interest to note that, as in the case of the α solution, no difference in the relative intensity of corresponding lines of the β solution may be detected in any of the photographs of B, C, and D—despite the changes in the dimensions of the structure due to solution.

The Mg_2Cu Phase.

The positions and relative intensities of the lines due to Mg_2Cu are the same, within experimental error, on all photographs in which they appear. Its crystal structure therefore remains unchanged in a series of alloys representing an extended range of composition.

The fundamental lattice, determined from measurements on the photographs obtained with alloy F (Table VIII.), was found to be hexagonal, with an axial ratio 3.464. The unit cell has a base of 5.281 Å.U. No reflexions are present which require a greater cell than this. The density 3.35 requires eight molecules in the unit cell. It is seen from Table VIII. that all lines on the film are satisfactorily accounted for by this structure.

The placing of the atoms within the cell is not possible from powder data alone, and additional measurements on single crystals are required to render the treatment complete.

Measurements on the films for alloys D and E corroborate the equilibrium diagram in that the lines of both β and Mg_2Cu phases are present on the same film. Analysis of these films was rather difficult as several lines of the two phases coincide. This was to be expected as both phases are built up of the same two kinds of atoms. Considerations of atomic radius would therefore lead one to expect that certain planes of both phases would have the same spacing. A careful examination of the film leads to the separation of the two sets of lines. This is facilitated by the fact that in the D photograph the β lines are most intense, while in that of E the Mg_2Cu predominate. Alloy E (Table VII.) gives a β lattice with $A_0 = 7.066$ Å.U. and an Mg_2Cu lattice of base 5.276 Å.U. The corresponding figures for the D alloy are 7.059 and 5.288 Å.U., which agree within the limits of accuracy of the measurements.

Magnesium.

The structure of magnesium has been shown by previous researches* to be close-packed hexagonal, with axial ratio 1.624. Table XI. gives measurements on the magnesium films corroborating this result and giving a base of length 3.206 Å.U., slightly smaller than the previously-accepted value of 3.22 Å.U.

* A. W. Hall, Proc. Nat. Acad. Soc. iii. p. 470; Owen & Preston, Proc. Phys. Soc. xxxv. p. 101.

TABLE VII.—Alloy E (36 per cent. Mg).

(Mixture of spinelle structure and hexagonal structure.)

Radiation.	hkl .	Intensity.	d/n observed.	d/n calculated.
K_{α}	10·0	M.	4·601	4·573
K_{α}	10·1	M.	4·441	4·436
K_{α}	10·2	M.	4·097	4·090
K_{α}	10·3	M.	3·663	3·658
K_{α}	$\left\{ \begin{array}{l} 10\cdot6 \\ 11\cdot2 \end{array} \right\}$	M.	2·544	$\left\{ \begin{array}{l} 2\cdot536 \\ 2\cdot534 \end{array} \right\}$
K_{α}	11·3	M.	2·312	2·423
K_{α}	$\left\{ \begin{array}{l} 00\cdot1 (8) \\ 10\cdot7 \end{array} \right\}$	St.	2·282	$\left\{ \begin{array}{l} 2\cdot286 \\ 2\cdot269 \end{array} \right\}$
* K_{α}	$\left\{ \begin{array}{l} 11\cdot5 \\ 131 \end{array} \right\}$	St.	2·137	$\left\{ \begin{array}{l} 2\cdot141 \\ 2\cdot128 \end{array} \right\}$
* K_{α}	$\left\{ \begin{array}{l} 10\cdot8 \\ 00\cdot1 (9) \\ 111 (2) \end{array} \right\}$	St.	2·042	$\left\{ \begin{array}{l} 2\cdot045 \\ 2\cdot032 \\ 2\cdot038 \end{array} \right\}$
K_{α}	10·9	W.	1·857	1·857
* K_{α}	100 (4)	V.W.	1·769	1·765
K_{α}	12·1	V.W.	1·714	$\left\{ \begin{array}{l} 1\cdot698 \\ 1\cdot721 \end{array} \right\}$
* K_{α}	$\left\{ \begin{array}{l} 12\cdot4 \\ 331 \end{array} \right\}$	W.	1·620	$\left\{ \begin{array}{l} 1\cdot616 \\ 1\cdot619 \end{array} \right\}$
K_{α}	12·5	V.W.	1·561	1·562
K_{α}	10·1 (3)	V.W.	1·474	1·478
K_{α}	12·7	M.	1·438	1·441
K_{α}	11·11	M.	1·406	1·407
* K_{α}	$\left\{ \begin{array}{l} 151 \\ 10\cdot2 (3) \end{array} \right\}$	M.	1·361	$\left\{ \begin{array}{l} 1\cdot358 \\ 1\cdot363 \end{array} \right\}$
K_{α}	30·7	M.	1·312	1·316
K_{α}	$\left\{ \begin{array}{l} 10\cdot6 (2) \\ 11\cdot2 (2) \end{array} \right\}$	V.W.	1·268	$\left\{ \begin{array}{l} 1\cdot268 \\ 1\cdot267 \end{array} \right\}$
K_{α}	110 (4)	M.	1·250	1·248
K_{α}	12·11	W.	1·195	1·198
K_{α}	22·7	V.W.	1·180	1·178
K_{α}	20·1 (2)	M.	1·138	1·343
K_{α}	30·11	V.W.	1·121	1·124
K_{α}	11·15	W.	1·106	1·107
* K_{α}	353	V.W.	1·077	1·077
* K_{α}	131 (2)	M.	1·065	1·064
* K_{α}	111 (4)	W.	1·019	1·019

NOTE.—Lines which include the β phase are marked with an asterisk (*).

TABLE VIII.—Alloy F (47 per cent. Mg).

(Hexagonal structure: $a = 5.281$ Å.U. axial ratio = 3.464.)

Radiation.	$h/k/l$.	Intensity.	d/n observed.	d/n calculated.
K_{α}	$\left\{ \begin{smallmatrix} 10.0 \\ 00.1 \end{smallmatrix} (4) \right\}$	M.	4.585	4.513
K_{α}	10.1	M.	4.420	4.436
K_{α}	10.2	V.W.	4.096	4.090
L_{α} (tungsten)	$\left\{ \begin{smallmatrix} 10.3 \\ 00.1 \end{smallmatrix} (5) \right\}$	V.W.	3.667	3.658
K_{α}	$\left\{ \begin{smallmatrix} 10.3 \\ 00.1 \end{smallmatrix} (5) \right\}$	M.	3.658	3.658
K_{α}	$\left\{ \begin{smallmatrix} 10.6 \\ 11.2 \end{smallmatrix} \right\}$	M.	2.537	$\left\{ \begin{smallmatrix} 2.536 \\ 2.533 \end{smallmatrix} \right\}$
K_{α}	11.3	M.	2.410	2.422
K_{α}	$\left\{ \begin{smallmatrix} 10.7 \\ 20.1 \end{smallmatrix} \right\}$	St.	2.276	2.269
K_{α}	$\left\{ \begin{smallmatrix} 11.5 \\ 20.3 \end{smallmatrix} \right\}$	M.	2.137	2.140
K_{α}	$\left\{ \begin{smallmatrix} 10.2 (2) \\ 00.1 (9) \end{smallmatrix} \right\}$	St.	2.037	$\left\{ \begin{smallmatrix} 2.045 \\ 2.032 \end{smallmatrix} \right\}$
K_{α}	$\left\{ \begin{smallmatrix} 11.7 \\ 10.9 \end{smallmatrix} \right\}$	M.	1.858	1.857
K_{α}	$\left\{ \begin{smallmatrix} 12.1 \\ 20.7 \end{smallmatrix} \right\}$	V.W.	1.713	$\left\{ \begin{smallmatrix} 1.720 \\ 1.698 \end{smallmatrix} \right\}$
K_{α}	$\left\{ \begin{smallmatrix} 12.4 \\ 10.4 (2) \end{smallmatrix} \right\}$	W.	1.616	1.616
K_{α}	$\left\{ \begin{smallmatrix} 12.5 \\ 10.11 \end{smallmatrix} \right\}$	M.	1.565	1.563
K_{α}	$\left\{ \begin{smallmatrix} 12.6 \\ 11.10 \end{smallmatrix} \right\}$	V.W.	1.498	1.504
K_{α}	10.1 (3)	W.	1.478	1.478
K_{α}	12.7	M.	1.438	1.441
K_{α}	10.5 (2)	M.	1.433	1.428
K_{α}	$\left\{ \begin{smallmatrix} 30.5 \\ 11.11 \\ 00.1 (13) \end{smallmatrix} \right\}$	M.	1.406	1.407
K_{α}	10.2 (3)	V.W.	1.364	1.363
K_{α}	$\left\{ \begin{smallmatrix} 10.13 \\ 20.11 \end{smallmatrix} \right\}$	V.W.	1.346	1.345
K_{α}	30.7	St.	1.315	1.316
K_{α}	00.1 (14)	St.	1.307	1.306
K_{α}	$\left\{ \begin{smallmatrix} 10.6 (2) \\ 11.2 (2) \end{smallmatrix} \right\}$	V.W.	1.266	$\left\{ \begin{smallmatrix} 1.268 \\ 1.266 \end{smallmatrix} \right\}$
K_{α}	12.11	V.W.	1.195	1.198

TABLE VIII. (*cont.*)

Radiation.	<i>h k l</i> .	Intensity.	<i>d/n</i> observed.	<i>d/n</i> calculated.
K_{α}	$\left\{ \begin{array}{l} 22\cdot7 \\ 10\cdot15 \end{array} \right\}$	V.W.	1·180	1·178
K_{α}	$\left\{ \begin{array}{l} 30\cdot10 \\ 31\cdot6 \end{array} \right\}$	V.W.	1·168	1·170
K_{α}	$\left\{ \begin{array}{l} 10\cdot7^{(2)} \\ 20\cdot1^{(2)} \end{array} \right\}$	M.	1·136	1·134
K_{α}	$\left\{ \begin{array}{l} 30\cdot11 \\ 40\cdot3 \end{array} \right\}$	W.	1·119	1·123
K_{α}	11·15	W.	1·106	1·107

TABLE IX.—Alloy G (54 per cent. Mg).

(Mixture of two hexagonal structures.)

Radiation.	<i>h k l</i> .	Intensity.	<i>d/n</i> observed.	<i>d/n</i> calculated
K_{β}	10·1	V.W.	4·421	4·436
K_{α}	10·0	M.	4·593	4·573
K_{α}	10·1	M.	4·434	4·436
K_{α}	10·2	V.W.	4·066	4·089
K_{α}	10·3	M.	3·658	3·658
* K_{α}	10·0	W.	2·779	2·777
* K_{α}	00·1 (2)	W.	2·611	2·603
* K_{α}	10·1	M.	2·452	2·450
K_{α}	11·3	M.	2·406	2·422
K_{α}	$\left\{ \begin{array}{l} 00\cdot1^{(8)} \\ 10\cdot7 \end{array} \right\}$	St.	2·278	$\left\{ \begin{array}{l} 2\cdot286 \\ 2\cdot269 \end{array} \right\}$
K_{α}	$\left\{ \begin{array}{l} 10\cdot2^{(2)} \\ 00\cdot1^{(9)} \end{array} \right\}$	St.	2·039	$\left\{ \begin{array}{l} 2\cdot045 \\ 2\cdot032 \end{array} \right\}$
* K_{α}	10·2	W.	1·898	1·899
K_{α}	10·9	M.	1·856	1·857
* K_{α}	11·0	W.	1·604	1·603
K_{α}	12·5	M.	1·564	1·563
* K_{α}	10·3	W.	1·471	1·472
K_{α}	12·7	M.	1·438	1·441
K_{α}	11·11	M.	1·403	1·406
K_{α}	10·2 (3)	W.	1·363	1·363
K_{α}	10·13	W.	1·340	1·344
K_{α}	30·7	M.	1·315	1·316
K_{α}	22·7	V.W.	1·179	1·178

NOTE.—Magnesium lines are denoted by an asterisk (*).

TABLE X.—Alloy H (82 per cent. Mg).

(Mixture of two hexagonal structures.)

Radiation.	$h k l$.	Intensity.	d/n observed.	d/n calculated.
K_{β}	10·1	W.	4·383	4·436
K_{α}	10·0	W.	4·593	4·573
K_{α}	10·1	W.	4·436	4·436
K_{α}	10·3	W.	3·663	3·658
* K_{β}	00·1 (2)	W.	2·593	2·603
* K_{α}	10·0	M.	2·785	2·776
* K_{β}	10·1	W.	2·424	2·449
* K_{α}	00·1 (2)	M.	2·608	2·603
K_{α}	$\left\{ \begin{array}{l} 10\cdot6 \\ 11\cdot2 \end{array} \right\}$	W.	2·532	$\left\{ \begin{array}{l} 2\cdot536 \\ 2\cdot533 \end{array} \right\}$
* K_{α}	10·1	St.	2·454	2·450
K_{α}	$\left\{ \begin{array}{l} 00\cdot1 (8) \\ 10\cdot7 \end{array} \right\}$	M.	2·278	$\left\{ \begin{array}{l} 2\cdot286 \\ 2\cdot268 \end{array} \right\}$
K_{α}	11·5	V.W.	2·138	2·140
K_{α}	$\left\{ \begin{array}{l} 10\cdot2 (2) \\ 00\cdot1 (9) \end{array} \right\}$	M.	2·039	$\left\{ \begin{array}{l} 2\cdot045 \\ 2\cdot032 \end{array} \right\}$
* K_{α}	10·2	M.	1·899	1·899
* K_{α}	11·0	M.	1·604	1·603
K_{α}	12·5	V.W.	1·567	1·562
* K_{α}	10·3	M.	1·471	1·471
* K_{α}	10·0 (2)	V.W.	1·387	1·388
* K_{α}	$\left\{ \begin{array}{l} 10\cdot2 (3) \\ 11\cdot2 \end{array} \right\}$	M.	1·363	$\left\{ \begin{array}{l} 1\cdot363 \\ 1\cdot365 \end{array} \right\}$
* K_{α}	20·1	M.	1·340	1·341
* K_{α}	00·1 (4)	W.	1·300	1·301
* K_{α}	10·1 (2)	W.	1·223	1·224
* K_{α}	10·4	W.	1·176	1·178
* K_{α}	20·3	W.	1·082	1·084
* K_{α}	12·1	W.	1·027	1·028
* K_{α}	11·4	W.	1·009	1·010
* K_{α}	10·5	W.	·9740	·9749
* K_{α}	12·3	W.	·8977	·8980

NOTE.—Magnesium lines are denoted by an asterisk (*).

The measurements for alloys G and H are given in Tables IX. and X. In both, the lines due to Mg_2Cu and magnesium appear having the same positions, within experimental error, as in the pure components.

As previously remarked, the variation of the dimensions of the magnesium lattice in these films is one in 3200. That of the Mg_2Cu lattice is one in 5280. The relative intensities of the lines also remain the same. If, therefore, there is any solution of magnesium in Mg_2Cu , and of copper in magnesium, the amount is so small as to be undetected by present methods.

The results of the present investigation, and, in particular, of the section dealing with the β phase, demonstrate the

TABLE XI.—Magnesium.
(Hexagonal closed packed.)

Radiation.	hkl .	Intensity.	d/n observed.	d/n calculated.
K_α	10·0	M.	2·785	2·777
K_α	00·1 (2)	M.	2·608	2·603
K_α	10·1	St.	2·454	2·450
K_α	10·2	M.	1·899	1·899
K_α	11·0	M.	1·603	1·603
K_α	10·3	M.	1·471	1·471
K_α	11·2	M.	1·364	1·365
K_α	20·1	M.	1·341	1·341
K_α	20·3	W.	1·081	1·084
K_α	12·1	W.	1·028	1·029
K_α	11·4	W.	1·010	1·011
K_α	12·2	W.	·9741	·9750
K_α	12·3	W.	·8980	·8980
K_α	30·2	V.W.	·8727	·8678

necessity for a thorough quantitative exploration of a system before the structure of any isolated phase may be determined with full knowledge of all the factors concerned. The simplicity of an equilibrium diagram obtained by metallurgical methods may not be trusted implicitly in such cases. A survey by X-ray analysis of the region on either side of the particular composition to be examined is therefore of primary importance to form the basis of a satisfactory investigation.

SUMMARY.

The copper-magnesium system of alloys has been investigated by the X-ray powder method.

Eight alloys were prepared, and their compositions were

determined by an electrolytic method—their densities by the suspension method.

X-ray powder photographs of each alloy were taken, and, with the procedure adopted, an accuracy of measurement of one in six hundred was obtainable.

The equilibrium diagram, due to Sahmen, was confirmed in its main features. Two new regions of solid solution were detected, viz. :—

(i.) The α phase—a solution of magnesium in the copper lattice up to approximately 3 per cent. magnesium.

(ii.) The β phase—a range of solution extending on either side of the composition represented by the formula Cu_2Mg . It is estimated that the β phase is confined to 2 or 3 per cent. on either side of the Cu_2Mg composition.

The α phase has a face-centred structure with a base varying from 3.610 Å.U. in copper to 3.634 Å.U. at the limit of solution.

The β phase has the face-centred spinelle structure, with eight molecules in the unit cell and having a base varying from 7.003 Å.U. to 7.059 Å.U., the dimensions increasing with increasing proportion of magnesium.

The Mg_2Cu phase was found to possess a hexagonal lattice of unvarying dimensions. The unit cell contains eight molecules with $a_0 = 5.281$ Å.U. and an axial ratio 3.464. In all other details Sahmen's diagram was verified. No trace of solid solution could be detected at the maximum end of the diagram.

The lattice constants of copper and magnesium were found to be copper $a_0 = 3.610$ Å.U. and magnesium $a_0 = 3.206$ Å.U. with axial ratio 1.624.

In conclusion, our thanks are due to Professors E. J. Evans and C. A. Edwards for facilities placed at our disposal for carrying out this research. We are also under obligation to Mr. Allen and Professor Taverner, of the Metallurgical Department, for advice and assistance in the preparation of the alloys.

APPENDIX.

Since the foregoing was written a publication on the copper-magnesium system by Westgren and his co-workers* has appeared.

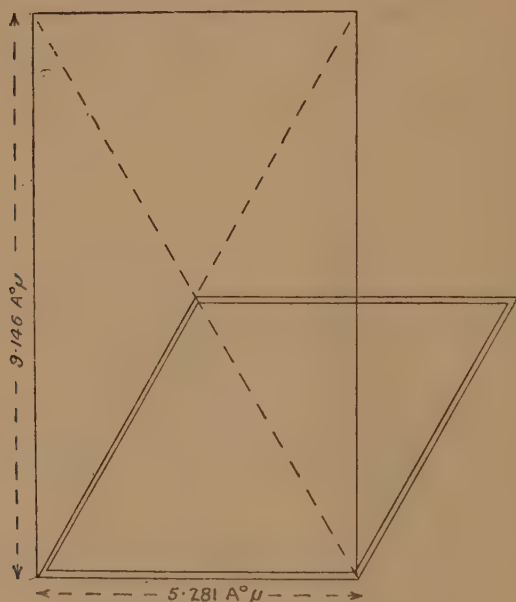
* *Zeit. Anorg. Chem.* Bd. clxxv. Heft 1-3 (1928).

1134 *X-Ray Investigation of Copper-Magnesium Alloys.*

The results of these authors are in general agreement with those described here, except apparently in the case of the crystal structure of Mg_2Cu . They found an orthorhombic arrangement of atoms for this alloy with a unit cell of edges $a_1=5.273 \text{ \AA.}$, $a_2=9.051 \text{ \AA.}$, and $a_3=18.21 \text{ \AA.}$ containing 16 molecules.

In the present investigation a hexagonal structure with unit cell of base 5.281 \AA. and height 18.29 \AA. was deduced

Fig. 4.



Mg_2Cu . Base of unit cell.

Single lines—Orthorhombic structure.

Double lines—Hexagonal structure.

Height is the same in both cases, 18.29 A.U.

containing eight molecules. A closer inspection reveals that the difference is one of the choice of axes. An orthorhombic cell of the above dimensions can be referred to hexagonal axes. If this is done, then the semi-diagonal of the base of the orthorhombic cell becomes a side of the base of the unit prism of the hexagonal arrangement (see fig. 4), giving a unit cell of one-half the volume of the first. The height is the same in both cases.

CXXVII. *The Frequency-Distribution of Examination Marks.*
By W. N. BOND, M.A., D.Sc., F.Inst.P., *Lecturer in*
Physics in the University of Reading *.

Summary.

It is shown that the frequency-distribution curves of the marks awarded to candidates in non-competitive examinations should not be of various extreme types if it is desired to arrange all the candidates so as to represent their order of merit and relative merit accurately. This implies that there is likely to be an optimum form of frequency-distribution curve, which the examiners should use their control to endeavour to obtain. A comparison of curves obtained in various examinations gives evidence that there is considerable consensus of opinion as to the desirable form of curve. It is shown that the mean curve deduced from these examinations approximates closely to a curve of simple mathematical form, which has probably more significance than a mere average.

THE frequency-distribution of the marks awarded to candidates in an examination is influenced by the range of attainment of the candidates, by the range of difficulty and type of the questions, by the method of marking, and by various kinds of error †. The frequency-distribution curve is therefore partly, but not completely, under the examiners' control.

If the range of questions is much wider than is required to test the range of candidates concerned, the curve will in general consist of an isolated hump at some point in the range of marks attainable. This hump will usually be sensibly symmetrical and of the normal Gauss's form ‡. The shape of the hump is here primarily influenced by the relative attainments of the candidates; the curve is rather analogous to that for a physical characteristic of the candidates, such as their height. The marks awarded in such an examination would appear to represent the relative merits of the candidates in the subject concerned, the per cent. mark at which the peak occurs having no absolute significance; but the result will be influenced by the errors of marking etc.

* Communicated by the Author.

† Edgeworth, Journ. Statistical Soc. 1888.

‡ Journ. Indian Math. Soc., April 1922; Encyc. and Dict. of Education, iv. p. 1593 (1922).

The maximum attainable mark being finite (say 100), the above type of examination would result, in an extreme case, in all the candidates receiving the same or almost the same mark. To avoid this defect it is therefore necessary to have a less wide range of questions. In fact it is desirable that every mark between 0 and 100 may at times be attained by some candidate. However, except for this broadening of the hump of the curve, the curve should be as nearly as possible unchanged in shape (so that the marks may still nearly represent the relative merit of the candidates, and not only their order of merit) *. The curve should therefore be, as a rule, nearly symmetrical about the 50-per-cent. mark. (In competitive examinations the better candidates may be arranged in order of merit more accurately by having the average mark attained less than 50 per cent., but this gives less accuracy in the ordering of the less successful candidates, and also makes the marks less representative of the relative merit of the candidates.)

Though it is advocated that the range of questions should not be too great for the range of capability of the candidates, on the other hand it is also necessary that the range of questions shall not be too limited in relation to the range of candidates. Thus, if the whole of a school were examined by questions of a standard suitable for a middle form (or if the highest form were examined entirely by questions of one type, such as problems in permutations and combinations), a double-humped curve might frequently result. The marks would then not represent the relative merit of the candidates, and would only facilitate the accurate placing of the medium candidates in order of merit.

With the curve thus limited (being approximately symmetrical, with a single hump somewhat like that of a normal Gauss's form and with a standard deviation that is neither too small nor too large), it appears likely that there is an optimum form of curve. At this stage we may consider the curves actually obtained in certain examinations. It is found † that in the subjects in which the marking is fairly determinate the different curves differ little, but that in the subjects in which "taste" affects the number of marks awarded, the curves have a smaller standard deviation and also differ appreciably from one another. For the purposes of the present investigation, data were collected for ten cases

* Not as advocated by B. C. Wallis (see 'Nature,' Dec. 29, 1928, p. 1013).

† Crofts and Jones, 'Secondary School Exam. Statistics,' pp. 51-2 (1928).

of subjects of the more determinate type. At least seven of these sets could be considered quite independent; and the cases were chosen where the average number of marks attained by a candidate was very nearly 50 per cent. School and University examinations were included, and the subjects comprised Elementary English and Arithmetic, Mathematics, Physics, Science subjects, Agriculture and Commerce. Equal "weight" was given to each of the ten sets. The mean values so deduced are given in the second line of Table I., and the individual sets are illustrated in the figure, in which the crosses correspond to the mean values. (In the

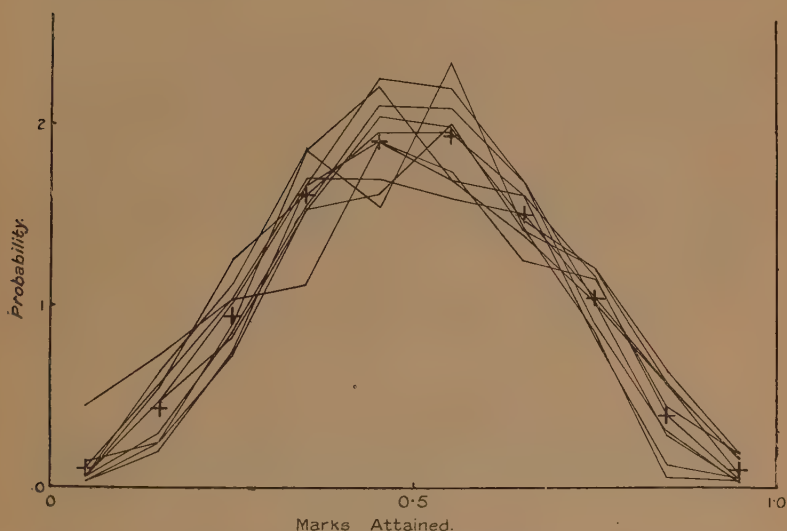


figure the average value of the probability in each interval is plotted.)

TABLE I.

Per cent. marks:—

0-9. 10-19. 20-29. 30-39. 40-49. 50-59. 60-69. 70-79. 80-89. 90-100.

Percentage of candidates:—

Observed:

1.0	4.3	9.4	16.1	19.1	19.4	15.1	10.5	4.0	1.0
± 0.2	± 0.4	± 0.5	± 0.4	± 0.5	± 0.5	± 0.4	± 0.4	± 0.5	± 0.2

Equation 1:

0.6	4.3	10.0	15.7	19.4	19.4	15.7	10.0	4.3	0.6
-----	-----	------	------	------	------	------	------	-----	-----

Equation 3:

1.0	4.5	9.9	15.5	19.1	19.1	15.5	9.9	4.5	1.0
-----	-----	-----	------	------	------	------	-----	-----	-----

Denoting the range of marks attainable by $x=0$ to $x=1$, for convenience, the peak of the curve at $x=0.5$ is found by interpolation to have a height $y=1.98 \pm 0.035$. The height of the peak in the corresponding determinate subjects given by Crofts and Jones * I estimate as 2.00 ± 0.03 (but the maximum is at about 45 per cent. marks).

These results show a considerable consensus of opinion, and also indicate that the curve is of simple form, as its maximum height is 1.99 ± 0.03 . The curve is to a first approximation a triangle; to a second approximation it may be represented by the equation :

$$y = 2 \sin^2 \pi x. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The values deduced from this equation are given in Table I. From the beginning it had been decided to compare the observed value with an extension of the "binomial" or "law of large numbers" form of curve. It was hoped that, not only might this law be found to represent the data satisfactorily, but also that the adjustable constants might be found to approximate to simple values. We may thus replace the binomial series of ordinates by a continuous curve :

$$y = A \cdot (n+2) \frac{\Gamma(n+2)}{\Gamma(n+2 \cdot x) \cdot \Gamma(n+2 \cdot 1-x)} \\ \times a^{(n+2)x-1} \cdot (1-a)^{(n+2)(1-x)-1} \quad . \quad (2)$$

In the present case $a=0.5$ by symmetry, n is found to be 2 (within the error of observation), and to make the area unity this requires $A=0.987$. The equation then reduces to

$$y = \frac{1.97_5}{\Gamma(4x) \cdot \Gamma(4 \cdot 1-x)}, \quad . \quad . \quad . \quad . \quad (3)$$

The results deduced from this equation are given in Table I. Equations (1) and (3) both fit the observations within the errors of observation. Prof. Pearson's Type IV. curve can be used to obtain about as good a fit, but is definitely empirical.

Whether either of equations (1) and (3) represents more than an empirical law or not, it appears likely that the observed values are approximating closely to a fundamental, simple, and fixed curve—which is the ideal to aim at in most examinations. Equations (1) and (3) represent smooth curves drawn through a set of equidistant ordinates that are

* *Loc. cit.*

proportional to 0, 1, 2, 1, 0, the area under the curve being unity ; the peak heights are 2.00 and 1.97₅ respectively.

I should like to thank Prof. J. A. Crowther and Miss I. E. Campbell for help in obtaining some of the data, and to say that this work was induced by that given in an earlier paper ("The Magnitude of Non-Dimensional Constants," *Phil. Mag.*, April 1929).

Department of Physics,
University of Reading,
April 6th, 1929.

CXXVIII. *Has the Temperature of Radiation any Effect on its Photographic Action?* By Dr. R. A. HOUSTOUN, Lecturer on *Physical Optics in the University of Glasgow* *.

u

IT is well known that when radiation is in equilibrium with matter in a cylinder it has the temperature of that matter. This is assumed in the proof of the Stefan-Boltzmann law of radiation and also in the proof of Wien's displacement law. If a hole is pierced in the cylinder, the radiation which issues has the same temperature which it had inside.

The temperature of a beam is not a property to which the experimental physicist has hitherto devoted attention, because he has regarded it as belonging rather to the source than to the beam itself. Planck, however, points out † that we distinguish between the "black body temperature" of the sun and its real temperature, and that the "black body temperature" of the sun, being the temperature of a black body emitting the same radiation as the sun, is a property of the radiation emitted and not of the sun at all ; consequently, it is more sensible to speak of the sun emitting radiation which possesses a temperature of so many degrees.

If we accept the principle of relativity, radiation has more "substance" than the space in which it is propagated, and it becomes easy to imagine its having temperature. We can then think with Planck of a point in space crossed by different beams of light each possessing its own temperature ; even the different colours in the same beam may have different temperatures. And the medium through which

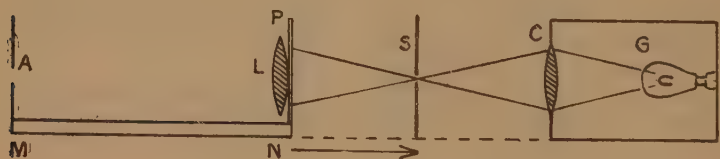
* Communicated by the Author.

† 'Theory of Radiation,' § 101.

the radiations are propagated may have a temperature quite different from any of them.

It occurred to me that the ability of a radiation to ionize a molecule or atom might depend on its temperature. The simplest way of putting the matter to test appeared to be to deliver two quantities of light of the same energy-content but different temperatures in the same time on equal adjacent areas of the same photographic plate. Photographic action is essentially a case of ionization. Of course the density of the photographic image has been regarded hitherto as due wholly to the intensity of the radiation and the time it acts, but an effect of temperature was never specifically looked for.

The figure represents the arrangement I have employed to carry out the test. The source of light was a 40-watt gas-filled lamp which was run off the 250-volt lighting circuit in series with a rheostat and milliammeter. The lamp was enclosed in a light-tight box. A lens in one side of the box focussed the filament on a hole in a brass plate S. The



diameter of this hole was either 4 mm. or 1.62 mm., so that only a small portion of the image was able to pass through. The rays diverged from the hole and fell on a ground-glass plate P, behind which was a lens L. The ground side of the glass was towards the lens. Both ground glass and lens were mounted at one end of a wooden base MN which could be moved up towards S. At the other end was fixed an aperture, exactly at the focus of the lens. Immediately behind this aperture was placed the photographic plate.

The lens was a biconvex one of focal length 27.9 cm., the radius of curvature being 28.16 cm. Hence its index of refraction was 1.5046. The distance through which MN was displaced was 16.7 cm. The diameter of the luminous disk on the ground glass PN was 5.8 cm.

Since the aperture A is at the focus of the lens, all the rays which are scattered in a direction parallel to the axis of the system arrive at A. Now suppose that the base MN moves up in the direction of the arrow towards S. The luminous disk in which the cone meets the plate contracts

to a point. After the displacement exactly the same quantity of light is scattered in a direction parallel to the axis of the system as before, and this light is brought to a focus by the lens at A. The base MN, it should be mentioned, ran along a guide from the one position to the other, and was on a different table from the lamp and screen S for fear that S might be disturbed by its motion. Thus in the one position the light came to A from a disk of diameter 5.8 cm.; in the other position the light came to A from a point or rather an extremely small area. In this second case, since the source appeared much brighter to an eye situated at A, it was emitting light of a higher temperature.

The distinction may be put in another way. In the first case a wide angle beam falls on the photographic plate; in the second case a narrow angle beam delivers the same quantity of energy in the same time on the plate. The change of angle involves at the same time a change in the profile of the wave-train, and I thought that this change of profile might be of decisive importance for ionization.

The statement that the same quantity of energy falls on A in the two cases requires slight corrections. Until the rays fall on the lens L, the losses are the same, but the high temperature light goes through a thicker part of the lens and falls on its surfaces and the surface of the photographic plate at A more normally.

The magnitude of these corrections can easily be calculated. The difference in the thickness of glass passed through is 0.03 cm. But according to W. D. Haigh* optical glass of the same refractive index as the lens used absorbs about 2 per cent. of the incident light per inch. Hence the correction due to different absorption in the glass is negligible.

The extreme ray of the wide angle pencil falls on the photographic plate at 6° with the normal. Fresnel's reflexion coefficients for this angle in the case of a medium of refractive index 1.5 are 0.2009 for the ray polarized in the plane of incidence, and 0.1981 for the ray polarized at right angles to the plane of incidence. The value for normal incidence is in each case 0.20000. Hence the difference is too small to affect the result. The difference will be smaller still in the case of the reflexion losses at the surfaces of the lens, for the angles of incidence are less there. Consequently, we can ignore them and assume that both beams deliver the same content of energy.

* *Proc. Opt. Conv.* 1926, p. 327.

The following table gives the details of the experiments made :—

List of Experiments.

Name of Plate.	Exposure.	° K.	° K.
Paget Slow Lantern	1 hour	1177	2000
	5 hours	1177	1850
Imperial Process	6 hours	970	1470
	17½ hours	970	1290
Wellington Ortho Process	10 min.	970	1470
	20 min.	1053	1560
	¾ hour	1177	1850
Imperial Special Sensitive	15 min.	1053	1670
	80 min.	1053	1560
Ilford Isozenith	10 min.	970	1470
	2 hours	970	1290
Imperial Panchromatic Process	30 min. red	970	1290
	17½ hours green .	970	1290
	10 min. red	970	1470
	20 min. green ...	1053	1670
Ilford Special Rapid Panchromatic	5 min. red	970	1290
	1 hour green ...	1053	1560
	1 min. red	970	1470
	8 min. green ...	1053	1670

The temperatures are those of the two radiations under comparison. They are in degrees Kelvin. The words red and green mean that in these cases either the Wratten standard tricolour red or green filter was placed in the path of the rays between the lens C and the aperture S.

The results of the experiments were wholly negative. There was a slight difference on two of the plates, but this was traced to a variation of the voltage during the experiment. As a rule a difference in density of 5 per cent. could have been detected. The plate-holder had an arrangement for exposing first one rectangle and then another rectangle alongside it, which was difficult to work. So sometimes the rectangles made good contact and sometimes they did not.

The temperatures were obtained from Wien's radiation formula

$$S = c_1 \lambda^{-5} e^{-c_2/\lambda T}.$$

If we confine ourselves to one wave-length, this gives

$$\log S/S_0 = \frac{c_2}{\lambda} \left(\frac{1}{T_0} - \frac{1}{T} \right).$$

Hence, if the ratio of the radiation is known for two temperatures, and one of these temperatures is known, the

other can be determined by means of the formula. It was assumed that, when the current through the lamp was diminished until the disk was just visible, the temperature of the radiation from the disk was 525°C . and the other temperatures calculated from this. They are, of course, only rough estimates. The ratio of the areas of disk and point was either about 1320 or about 3300.

There does not seem to be any method of greatly increasing the sensitiveness of the test.

CXXIX. *Heat Flow when the Boundary Condition is Newton's Law.* By J. H. AWBERY, B.A., B.Sc., *Physics Department, The National Physical Laboratory, Teddington, Middlesex* *.

ABSTRACT.

THE general problem of a body from which the heat loss at one or more surfaces is proportional to the excess temperature at the point, over that of the air, is considered with reference to those cases where the final steady state is not one of uniform temperature.

Two illustrative cases are worked out :—

- (41) The case of a cable buried in the ground.
- (42) The case of a conducting girder projecting into a layer of insulation.

1. Introduction.

THE standard text-books on heat conduction usually consider one or two problems of the cooling of bodies under the condition that the heat loss from the surface is proportional to the temperature at the point considered; attention seems to be restricted, however, to problems of variable temperature, in which the initial state is given, and the final state is one of uniform temperature throughout.

It is the object of the present paper to consider the class of problems where there is a constant supply of heat at some point, line, or surface, so that the steady state reached is one in which there is a definite temperature distribution, other than a uniform distribution of heat.

* Communicated by the Author.

2. General Considerations.

To each such problem corresponds another in which the boundary condition is replaced by the simpler one of an isothermal surface. If the latter problem is directly soluble by Fourier analysis, then the original one will, in general, be soluble by the same method, so that we need devote no attention to the case.

Consider, however, a problem where the solution of the corresponding isothermal case has been obtained by images, or conjugate functions, or some other method, with the result

$$v_1 = f(x, y, z),$$

where v_1 is the temperature at any point, when the isothermal boundary condition applies.

If we form the expression

$$v = v_1 + v_2,$$

where v_2 satisfies

$$\nabla^2 v_2 = 0,$$

everywhere except possibly at the heat source, v will satisfy the Laplace equation. Moreover, at the boundary under consideration v_1 has been constructed to vanish, so that v reduces to v_2 , and the heat flow at this boundary to

$$-K \frac{\partial v}{\partial n} \equiv -K \left(\frac{\partial v_1}{\partial n} + \frac{\partial v_2}{\partial n} \right),$$

where n represents the outward-drawn normal to the boundary, and K is the thermal conductivity of the medium.

The expression of Newton's law is

$$Ev = -K \partial v / \partial n,$$

so that the boundary condition reduces to

$$-K \left(\frac{\partial v_1}{\partial n} + \frac{\partial v_2}{\partial n} \right) = Ev_2. \quad . \quad . \quad . \quad (1)$$

The first term is known, since v_1 is a known function of position, so that equation (1) is a differential equation, imposing a condition on v_2 . If the physical problem is a definite one, the equations of type (1), at all the boundaries, together with the fact that v_2 is harmonic, are clearly sufficient to define v_2 . (It may happen, however, that the condition at some boundaries will be Newton's law, and at

others the isothermal condition will hold. This involves no extra difficulty.)

In general, the method of conjugate functions will not determine v_1 in the form postulated above (*i. e.*, as an explicit function of position). It is essentially a method for use in two dimensions, and it gives an equation of the form

$$w_1 = f(z), \quad (2)$$

where $w_1 = v_1 + iu_1$, $z = x + iy$, and $u_1 = k$ is the equation to the orthogonal surfaces of v_1 , whilst $i = \sqrt{-1}$. (z is to be distinguished from the z previously used.) In this case the boundary condition remains of the form (1), but v_1 has now to be evaluated from the equation (2) before it can be substituted in (1). If we restrict consideration to the case where the boundary concerned is straight, the axes can always be selected so that this boundary becomes the line $y = 0$. Then,

since $w_1 = f(z)$, the quantity to be evaluated is $\left(\frac{\partial v_1}{\partial y}\right)_{y=0}$.

Even if the relation (2) cannot be separated into two equations, this evaluation can frequently be carried out; for differentiating the implicit equation (2), setting $dx = 0$ and $y = 0$, the value of $\partial w_1 / \partial y$ is obtained. But

$$w_1 = u_1 + iv_1,$$

so that

$$\frac{\partial w_1}{\partial y} = \frac{\partial u_1}{\partial y} + i \frac{\partial v_1}{\partial y}$$

and the quantity required is the imaginary part of $\partial w_1 / \partial y$, which will be of a simpler form than the original equation.

One case requires particular notice. The function to be taken in (2), to solve a given problem by the method of conjugate functions is frequently found by transferring the boundary on to the real axis of a subsidiary t plane. In these cases the equation (2) is replaced by

$$\left. \begin{aligned} w &= F(t) \\ z &= G(t) \end{aligned} \right\}, \text{ where } F \text{ and } G \text{ are known functions.}$$

It does not appear that the generalization from the isothermal to the Newton's law problem can be carried out in practice, in this case, unless t can be eliminated from the above pair of equations.

We propose to illustrate the method by working out two cases which present themselves in practice.

(1) A cable is buried in the ground, the heat loss from the latter being given by Newton's law. Mathematically,

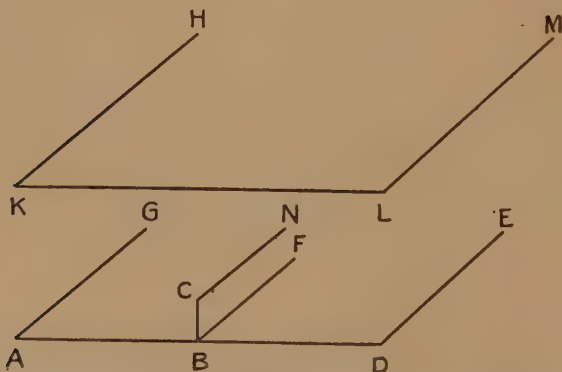
we shall represent this problem by that of a line-source in a semi-infinite medium, with one plane face to which the line-source is parallel.

(2) The case of a girder projecting into insulation. This is shown in fig. 1. We take the plane GADE, and the girder NCBF, as being rigorously at one and the same temperature; whilst the plane HKLM is the one from which heat loss is governed by Newton's law. Both planes extend to infinity in all directions, and the intervening space is filled with a homogeneous conducting medium.

3. Example I.—Cable buried in the Ground.

The solution of the corresponding problem when the ground is an isothermal at temperature v_0 is easily obtained

Fig. 1.



by the method of images. Taking the surface of the ground as the plane $y=0$, and taking the plane $x=0$ as the perpendicular to the ground through the cable, the temperature at (x, y) is

$$v_1 = v_0 + \frac{Q}{4\pi K} \log \left(\frac{x^2 + y - a^2}{x^2 + y + a^2} \right),$$

where Q is the heat generation per second per cm. length of the cable, K is the thermal conductivity of the ground, and a is the depth of the cable below the surface.

For the case to be investigated, we take then

$$v = \frac{Q}{4\pi K} \log \left(\frac{x^2 + y - a^2}{x^2 + y + a^2} \right) + v_2,$$

where v_2 is harmonic, and v_0 has been taken as 0, which

merely involves a change in the origin for temperature measurements.

In Cartesian coordinates a known solution of $\nabla^2 v_2 = 0$ is

$$v_2 = (\alpha e^{ny} + \beta e^{-ny})(\gamma \cos nx + \delta \sin nx),$$

and to avoid infinite temperatures as the depth increases, we must take $\beta = 0$. We shall also find that the term in $\sin nx$ is unnecessary, so that we adopt $Ae^{ny} \cos nx$ as our fundamental solution. The limit of a series of such terms is

$$v_2 = \int_0^\infty A e^{\lambda y} \cos \lambda x d\lambda,$$

which satisfies $\nabla^2 v_2 = 0$ and does not become infinite within the region we consider ($-\infty < y < 0$).

Consequently, the problem will be solved if we take

$$v = \frac{Q}{4\pi K} \log \left(\frac{x^2 + y - a^2}{x^2 + y + a^2} \right) + \int_0^\infty A e^{\lambda y} \cos \lambda x d\lambda \quad (\text{IV.})$$

with a suitable value of A .

When $y = 0$, this becomes

$$v = \int_0^\infty A \cos \lambda x d\lambda,$$

whilst $(\partial v / \partial y)_{y=0}$ is

$$-\frac{aQ}{\pi K(x^2 + a^2)} + \int_0^\infty A \lambda \cos \lambda x d\lambda.$$

The boundary condition $-K \partial v / \partial y = Ev$ will thus be satisfied if

$$\int_0^\infty (E + K\lambda) A \cos \lambda z d\lambda = \frac{aQ}{\pi(x^2 + a^2)} \dots \quad (\text{V.})$$

Now by Fourier's Integral Theorem,

$$\frac{aQ}{\pi(x^2 + a^2)} = \frac{2}{\pi} \int_0^\infty \int_0^\infty \frac{aQ \cos \lambda x \cos \gamma \lambda}{\pi(\gamma^2 + a^2)} d\lambda d\gamma. \quad (\text{V. } a)$$

Thus we must identify the integrals in (V. a) and (V.), and this gives

$$A = \frac{2aQ}{\pi^2(E + K\lambda)} \int_0^\infty \frac{\cos \lambda \gamma d\gamma}{\gamma^2 + a^2}.$$

Substituting for A in (IV.), we reach the solution

$$v = \frac{Q}{4\pi K} \log \left(\frac{x^2 + y - a^2}{x^2 + y + a^2} \right) + \frac{2aQ}{\pi^2} \int_0^\infty \int_0^\infty \frac{e^{\lambda y} \cos \lambda x \cos \lambda \gamma}{(E + K\lambda)(\gamma^2 + a^2)} d\lambda d\gamma.$$

4 F 2

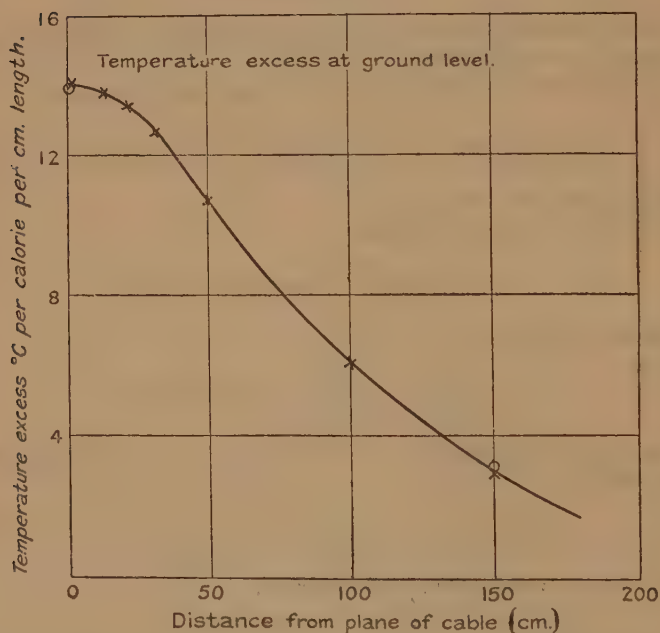
The integration with regard to γ , viz.,

$$\int_0^\infty \frac{\cos \lambda \gamma}{\gamma^2 + a^2} d\gamma,$$

may be carried out. It reduces to $\frac{\pi e^{-a\lambda}}{2a}$, so that the final expression is

$$v = \frac{Q}{4\pi K} \log \left(\frac{x^2 + y - a^2}{x^2 + y + a^2} \right) + \frac{Q}{\pi} \int_0^\infty \frac{e^{\lambda(y-a)} \cos \lambda x}{E + K\lambda} d\lambda.$$

Fig. 2.



I have not succeeded in reducing this integral further, but it may easily be evaluated numerically by plotting the integrand and measuring the area of the curve with a planimeter. Or it could possibly be expanded as a series in λ .

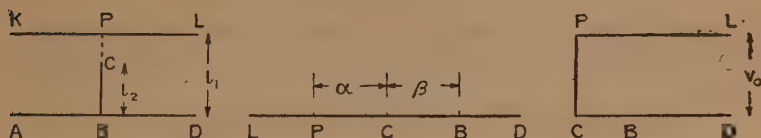
The temperatures on the ground, where $y=0$ and the first term vanishes, were calculated for the case $a=76$ cm. (*i. e.*, about 2 ft. 6 in.), $Q=1$, $E=0.00025$, $K=0.0045$, and the results are shown in fig. 2. They were calculated by quadratures, using Simpson's rule with 11 ordinates, and checked at the first and last of the calculated points by using 27 ordinates.

Since the excess in temperature immediately over the cable is proportional to Q , its actual value may easily be deduced for a cable buried 2 ft. 6 in. in ground of about these thermal characteristics. For an ordinary 3-core cable of diameter 0.15 in. and carrying 150 amp., Q is approximately $1/30$ calorie (per cm. run per sec.), so that the temperature excess will be $1/30$ of that shown in the figure (for which $Q=1$).

4. Example II. — Girder projecting into Insulation.

We must solve first the corresponding problem with the boundary as an isothermal. In fig. 3 the left-hand portion shows a section perpendicular to the girder; DBA and CB are to be one isothermal, and KL another. It is obvious by symmetry that CP will be a line of heat flow. The diagram on the right of fig. 3 is the corresponding diagram, in the w plane, where $w=u+iv$, u being the flow function and

Fig. 3.



v the temperature. To transform the one diagram into the other, we represent each conformally on the real axis in the " t " plane (centre portion of diagram, lettered similarly to the others).

The equations for the transformations are given by the Schwarz-Christoffel theorem* and take the forms

$$\frac{dz}{dt} = A(t+\alpha)^{-\frac{1}{2}}(t-\beta)^{-\frac{1}{2}},$$

$$\frac{dw}{dt} = B(t+\alpha)^{-\frac{1}{2}}t^{-\frac{1}{2}},$$

of which the solutions are

$$z = A \cosh^{-1} \left(\frac{2t+\alpha-\beta}{\alpha+\beta} \right) + C, \quad \dots \quad (\text{I.})$$

$$w = B \cosh^{-1} \left(\frac{2t+\alpha}{\alpha} \right) + D. \quad \dots \quad (\text{II.})$$

* Forsyth, 'Theory of Functions,' 3rd edition, p. 665.

The constants of integration will be chosen so that $C=D=0$ and

$$A = l_1/\pi, \quad B = v_0/\pi. \quad \text{. . . . (III.)}$$

This involves taking B as origin in the z plane, and C in the w plane. It introduces the known constants l_1 and v_0 , the width of the strip, and the temperature difference across it, as marked in the diagram. The remaining quantity which is known *a priori*, viz., l_2 , the depth of the girder, is related to α/β by the equation

$$\pi l_2 = -il_1 \cosh^{-1}(\alpha - \beta)/(\alpha + \beta).$$

Using (III.), the result of eliminating t between (I.) and (II.) is

$$\alpha \left(\cosh \frac{w\pi}{v_0} - 1 \right) = (\beta - \alpha) + (\beta + \alpha) \cosh \pi z/l_1. \quad \text{(IV.)}$$

Now, since $w = u + iv$, $z = x + iy$, the real and imaginary parts of this equation may be separated and equated independently. The result is

$$\alpha \left(\cosh \frac{u\pi}{v_0} \cos \frac{v\pi}{v_0} - 1 \right) = (\beta - \alpha) + (\beta + \alpha) \cosh \pi x/l_1 \cos \pi y/l_1, \quad \text{. . . (V.)}$$

$$\alpha \sinh \frac{u\pi}{v_0} \sin \frac{v\pi}{v_0} = (\beta + \alpha) \sinh \pi x/l_1 \sin \pi y/l_1. \quad \text{(VI.)}$$

In the present problem, u may be eliminated at this stage by using the relation

$$\cosh^2 \theta - \sinh^2 \theta = 1,$$

and this leads to the single equation

$$\begin{aligned} \cos^2 \frac{\pi v}{v_0} \sin^2 \frac{\pi v}{v_0} &= \beta^2 \sin^2 \frac{\pi v}{v_0} + (\alpha + \beta)^2 \sin^2 \frac{\pi v}{v_0} \cosh^2 \frac{\pi x}{l_1} \cos^2 \frac{\pi y}{l_1} \\ &+ 2\beta(\alpha + \beta) \sin^2 \frac{\pi v}{v_0} \cosh \frac{\pi x}{l_1} \cos \frac{\pi y}{l_1} \\ &- (\alpha + \beta)^2 \cos^2 \frac{\pi v}{v_0} \sinh^2 \frac{\pi x}{l_1} \sin^2 \frac{\pi y}{l_1}. \quad \text{(VII.)} \end{aligned}$$

This is the (implicit) equation for v_1 , referred to in paragraph 2. By its construction, v reduces to v_0 when $y = l_1$, i. e., over the upper surface of the strip.

To solve the generalized problem, where Newton's law holds over the upper surface, we shall, following the procedure outlined in paragraph 1, add to v a quantity v_2 which

is harmonic and vanishes over the lower boundary, but such that $(v+v_2)$ obeys Newton's law over the upper boundary.

To satisfy the first two conditions, we may take

$$v_2 = A \int_0^\infty \sinh my \sin mx \, dm,$$

so that

$$\frac{\partial v_2}{\partial y} = A \int_0^\infty m \cosh my \sin mx \, dm. \quad (\text{VIII.})$$

Before imposing the third condition, we must evaluate $(\partial v / \partial y)_{y=l_1}$ from equation (VII.). On differentiating that equation, we obtain, after some reduction :

$$\begin{aligned} & \frac{1}{v} \frac{\partial v}{\partial y} \sin \frac{\pi v}{v_0} \cos \frac{\pi v}{v_0} \\ & \left[\alpha^2 \cos^2 \frac{\pi v}{v_0} - \alpha^2 \sin^2 \frac{\pi v}{v_0} - (\alpha + \beta)^2 \cosh^2 \frac{\pi x}{l_1} \cos^2 \frac{\pi y}{l_1} \right. \\ & \quad \left. - \beta^2 - 2\beta(\alpha + \beta) \cosh \frac{\pi x}{l_1} \cos \frac{\pi y}{l_1} \right. \\ & \quad \left. - (\alpha + \beta)^2 \sinh^2 \frac{\pi x}{l_1} \sin^2 \frac{\pi y}{l_1} \right] \\ & = -\frac{1}{l_1} \sin \frac{\pi y}{l_1} \left[\sin^2 \frac{\pi v}{v_0} \right. \\ & \quad \left\{ (\alpha + \beta)^2 \cosh^2 \frac{\pi x}{l_1} \cos \frac{\pi y}{l_1} + \beta(\alpha + \beta) \cosh \frac{\pi x}{l_1} \right\} \\ & \quad \left. + \cos^2 \frac{\pi v}{v_0} \left\{ (\alpha + \beta)^2 \sinh^2 \frac{\pi x}{l_1} \cos \frac{\pi y}{l_1} \right\} \right]. \end{aligned}$$

We cannot obtain the value of $(\partial v / \partial y)_{y=l_1}$ immediately from this equation, since at $y=l_1$ the factors $\sin \pi v / v_0$ and $\sin \pi y / l_1$ on the two sides of the equation, vanish. The limit of their ratio may be evaluated in the form

$$\frac{d(\sin \pi y / l_1)}{d(\sin \pi v / v_0)} = \frac{v_0}{l_1} \left(\frac{\partial v}{\partial y} \right)_{y=l_1},$$

and then (setting $v=v_0$, $y=l_1$ with this value for the limit

of $\frac{\sin \pi y / l_1}{\sin \pi v / v_0}$) we obtain $\left(\frac{\partial v}{\partial y} \right)_{y=l_1}$ in the form

$$\frac{v_0(\alpha + \beta) \sinh \pi x / l_1}{\sqrt{[\beta - (\alpha + \beta) \cosh \pi x / l_1]^2 -}}$$

(As a check to the algebra, the same value of the limit was obtained by determining it directly from the undifferentiated equation (VII.). We are now in a position to satisfy the equation expressing Newton's law,

$$E(v + v_2 - v_0) = -K \left(\frac{\partial v_1}{\partial y} + \frac{\partial v_2}{\partial y} \right) \quad \text{at } y = l_1,$$

where v_0 is now taken as the air temperature above the strip. Substituting the values of v , v_2 and their derivatives from (VII.), (VIII.), and (IX.), and writing $\mu(x)$ to represent $\sqrt{[\beta - (\alpha + \beta) \cosh \pi x/l_1]^2 - \alpha^2}$, this becomes

$$\begin{aligned} EA \int_0^\infty \sinh ml_1 \sin mx \, dm \\ = -K \left[\frac{v_0(\alpha + \beta) \sinh \pi x/l_1}{\mu(x)} + A \int_0^\infty m \cosh ml_1 \sin mx \, dm \right]. \end{aligned}$$

Rearranging this equation, it becomes

$$\begin{aligned} -A \int_0^\infty \sin mx (E \sinh ml_1 + Km \cosh ml_1) \, dm \\ = \frac{Kv_0(\alpha + \beta) \sinh \pi x/l_1}{\mu(x)}, \end{aligned}$$

and by Fourier's Theorem, the right-hand side is

$$\frac{2}{\pi} \int_0^\infty \int_0^\infty \frac{Kv_0(\alpha + \beta) \sinh \pi \lambda/l_1 \sin m\lambda \sin mx}{\mu(\lambda)} \, d\lambda \, dm.$$

Thus A must be taken as

$$-\frac{2}{\pi} \int_0^\infty \frac{Kv_0(\alpha + \beta) \sinh \pi \lambda/l_1 \sin m\lambda}{\mu(\lambda) [E \sinh ml_1 + Km \cosh ml_1]} \, d\lambda,$$

and the final result is :

$$\text{Temperature at } (x, y) = v + v_2,$$

where v is given by equation (VII.) and

$$\begin{aligned} & \frac{2v_0K(\alpha + \beta)}{\pi} \\ & \int_0^\infty \frac{\sinh \pi \lambda/l_1 \sin m\lambda \sinh my \sin mx \, dm \, d\lambda}{[E \sinh ml_1 + Km \cosh ml_1]} \\ & \sqrt{[\beta - (\alpha + \beta) \cosh \pi \lambda/l_1]^2 - \alpha^2} \end{aligned}$$

It may be useful to collect here the meanings of the symbols occurring in this final result :—

v_0 = temperature of upper air, immediately over the strip;

l_1 = width of strip, so that upper surface is $y=l_1$;

E = heat loss per unit area per sec. per 1° excess above the air temperature ;

K = thermal conductivity of the material in the strip.

α, β (which only occur in the form of their ratio) are connected with the depth of the girder (l_2) by the equation

$$\pi l_2 = -l_1 \cosh^{-1} (\alpha - \beta) / (\alpha + \beta).$$

This final result is mathematically a complete solution to the problem which we set out to investigate, but since it is in the form of a double integral, it is not suitable for numerical application.

It is probably permissible to infer, since a comparatively simple problem leads to such a complex result, that the method given in this paper, although providing the general solution of the problem presented in the title, does not do so in a form suitable to the physicist. It is, however, the only discussion I have seen of the problem, and if in any physical application a result in *numerical* form is required, the resulting solution will have to be dealt with further in whatever manner is convenient, depending on the particular problem considered.

CXXX. *A Simple Proof and an Extension of Heaviside's Operational Calculus for Invariable Systems.* By BALTH. VAN DER POL, D.Sc. *.

§1. **I**N his book, 'Electromagnetic Theory,' which was published in the 'nineties of last century, Heaviside devised and made an extensive use of an operational method which enabled him to write down almost immediately the disturbance in any linear electrical (or mechanical) system resulting from the sudden application at the time $t=0$ of a given force. The system was supposed to be stable and, for $t < 0$, to be in complete rest, *i. e.*, at first the coordinates with all their derivatives were supposed to be zero.

* Communicated by the Author.

As a direct formal proof for the two important theorems deduced by Heaviside by means of his operational calculus was not given by him, some proofs were given at a later date by several writers.

The problem to which we will restrict ourselves in the present paper is that of the solution of a set of simultaneous linear differential equations with constant coefficients (representing therefore an invariable system) all the right-hand members of which are zero, except one, which represents the application of the given force. To begin with, we shall take for this force Heaviside's "unit function," which is defined as equal to zero for $t < 0$ and unity for $t > 0$.

Two solutions of practically the same nature, both leading up to the Heaviside symbolic solution of this problem, were published independently at practically the same date by Karl Willy Wagner* and by T. J. I'A. Bromwich†. Both authors analyse the "unit function," which we will denote by [1], in the complex Fourier integral :

$$[1] = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \frac{e^{\nu t}}{\nu} d\nu. \quad . \quad . \quad . \quad . \quad (1)$$

Thereupon the response of the linear system to each of the frequencies ν could easily be obtained, and a final integration of all these responses to the individual frequencies of the continuous spectrum yielded the solution of the problem, the path of integration in the complex plane corresponding to the initial conditions of complete rest.

Bromwich's work is fully expounded in a book recently published by H. Jeffreys‡.

Moreover, a proof was also given by J. R. Carson in 1917§, who reduced the operational method to the solution of an integral equation. Carson and Heaviside himself applied the operational method to numerous problems connected with the propagation of disturbances over a cable, and a clear exposition of the whole matter based on his integral equation is to be found in Carson's book||. For further literature on this subject the reader may be referred to the books by Jeffreys and Carson. However, a very important

* *Arch. f. Electrotechnik*, iv. p. 159 (1916).

† *Proc. London Math. Soc.* xv. p. 401 (1916).

‡ H. Jeffreys, 'Operational Methods in Mathematical Physics' (Cambridge University Press, London, 1927).

§ *Phys. Rev.* x. p. 217 (1917).

|| J. R. Carson, 'Electric Circuit Theory and the Operational Calculus' (McGraw-Hill Book Co., Inc., New York, 1926).

contribution to our subject-matter, to which no reference is to be found yet in the books just mentioned, is contained in a little pamphlet of 20 pages by P. Lévy*, who deduces the Heaviside operational calculus with the aid of Volterra's "*produit de composition*" of two functions, $f(t)$ and $g(t)$, which is written $f*g$ and defined as

$$f*g = \int_0^t f(\tau) \cdot g(t-\tau) d\tau. \quad . \quad . \quad . \quad (2)$$

In fact, Lévy points out that the solution of Carson's integral equation is given by the complex integral of Wagner and Bromwich, so that in Lévy's work the two originally divergent routes meet again†.

It is the purpose of the present paper to give a very simple proof of the two operational solutions (first given by Heaviside and already referred to above) of the disturbance in an invariable linear system following upon the application of a "unit force" while the system was initially at rest. Our method enables us also easily to extend the solution to cases where the system originally is not at rest, and, moreover, where the force, which is suddenly applied at the time $t=0$, is not a constant but an arbitrary function of the time. In a later paper we hope to extend these considerations to equations with variable coefficients.

§ 2. Let us, in order to simplify the problem as much as possible, first consider the single differential equation

$$a_0^{(n)} y + a_1^{(n-1)} y + a_2^{(n-2)} y + \dots + a_n y = [1], \quad . \quad . \quad (3)$$

where $y^{(n)}$ is written for $\frac{d^n y}{dt^n}$. Let, further, the initial conditions be given as

$$\text{for } t < 0: \quad y^{(1)} = y^{(2)} = y^{(n-1)} = y = 0; \quad . \quad . \quad . \quad (4)$$

and let it further be assumed that the solutions are stable so that none of the roots have a positive real part. We observe that in this case, as in many others, it is much simpler to

calculate $\int_0^\infty e^{-pt} y dt$ than y itself. For, in order to evaluate

* Paul Lévy, 'Le Calcul symbolique d'Heaviside' (Gauthier-Villars, Paris, 1926). I am indebted to Dr. Le Corbeiller, of Paris, for drawing my attention to Lévy's work on the subject, which was also published in the *Bulletin des Sciences Mathématiques*.

† See also March, Bull. Am. Math. Soc. xxxiii, p. 311 (1927).

this integral, we multiply (3) by e^{-pt} and integrate between the limits zero and infinity. A typical term,

$$\int_0^{\infty} e^{-pt} y^{(\rho)} dt,$$

thus arising can easily be reduced by partial integrations by the aid of the initial conditions (4), for

$$\begin{aligned} \int_0^{\infty} e^{-pt} y^{(\rho)} dt &= \left[e^{-pt} y^{(\rho-1)} \right]_0^{\infty} + p \int_0^{\infty} e^{-pt} y^{(\rho-1)} dt \\ &= 0 + p \int_0^{\infty} e^{-pt} y^{(\rho-1)} dt. \end{aligned}$$

By repeatedly integrating by parts we thus obtain

$$\int_0^{\infty} e^{-pt} y^{(\rho)} dt = p^{\rho} \int_0^{\infty} e^{-pt} y dt.$$

The right-hand member similarly becomes

$$\int_0^{\infty} [1] e^{-pt} dt = \int_0^{\infty} e^{-pt} dt = \frac{1}{p}.$$

Thus we obtain from (3):

$$\{a_0 p^n + a_1 p^{n-1} + a_2 p^{n-2} + \dots + a_n\} \int_0^{\infty} e^{-pt} y dt = \frac{1}{p}. \quad (5)$$

If we call the polynomial

$$a_0 p^n + a_1 p^{n-1} + a_2 p^{n-2} + \dots + a_n = H(p),$$

we thus find immediately

$$\int_0^{\infty} e^{-pt} y dt = \frac{1}{pH(p)}, \quad \dots \quad (6)$$

which is Carson's integral equation.

We notice that the polynomial $H(p)$ of the left-hand member of (5) has exactly the same form as the left-hand member of our differential equation (3), except that $\frac{d^m}{dt^m}$ has been replaced by p^m . Thus the idea of operational solution arises, although p is nothing until now but an ordinary positive number.

So far, instead of having solved for y we have obtained an expression for $\int_0^{\infty} e^{-pt} y dt$ only. In all cases, however, where y can be expanded in a series of positive powers of t

the deduction of y from (6) is a simple matter; for let us assume y to be

$$y = b_0 + b_1 t + b_2 t^2 + b_3 t^3 + \dots,$$

the integral of (6) then becomes

$$\int_0^\infty e^{-pt} y dt = \frac{1}{p} \left[b_0 + \frac{1!}{p} b_1 + \frac{2!}{p^2} b_2 + \frac{3!}{p^3} b_3 + \dots \right]. \quad (7)$$

by virtue of the definition of the Gaussian Π -function :

$$\int_0^\infty e^{-pt} t^n dt = \frac{1}{p} \frac{\Pi(n)}{p^n},$$

which, for integral positive values of n , becomes

$$= \frac{1}{p} \cdot \frac{n!}{p^n}.$$

If, therefore, we expand the right-hand member of (6) in a series of negative powers of p :

$$\frac{1}{pH(p)} = \frac{1}{p} \left(c_0 + \frac{c_1}{p} + \frac{c_2}{p^2} + \frac{c_3}{p^3} + \dots \right), \quad \dots \quad (8)$$

and identify the corresponding terms of (7) and (8), we obtain :

$$b_0 = c_0,$$

$$c_1 = \frac{1!}{1!} b_1,$$

$$b_2 = \frac{c_2}{2!},$$

$$b_3 = \frac{c_3}{3!},$$

$$\vdots$$

$$b_m = \frac{c_m}{m!}.$$

We thus find :—

Heaviside's power series expansion or Operational Theorem.
No. 1 :

Write in the differential equation p^m instead of $\frac{d^m}{dt^m}$. Thus obtain $H(p)$. Expand $1/H(p)$ in powers of p^{-1} :

$$\frac{1}{H(p)} = c_0 + \frac{c_1}{p} + \frac{c_2}{p^2} + \dots;$$

write further $t^m/m!$ instead of p^{-m} , and the resulting expression

$$y = c_0 + c_1 \frac{t}{1!} + c_2 \frac{t^2}{2!} + c_3 \frac{t^3}{3!} + \dots$$

is the solution of the differential equation for a "unit" applied force with the initial condition of complete rest.

We may write this result symbolically

$$y = \frac{1}{H(p)} \cdot \dots \dots \dots (9)$$

Moreover, Heaviside also gave another solution, leading up to Expansion theorem No. 2. Starting again from (6),

$$\int_0^\infty e^{-pt} y dt = \frac{1}{pH(p)}, \dots \dots \dots (6)$$

we expect, from the nature of the problem, that y can also be written as follows :

$$y = C_0 + C_1 e^{p_1 t} + C_2 e^{p_2 t} + \dots + C_n e^{p_n t}, \dots (10)$$

where the p 's are the roots of $H(p) = 0$.

Substituting (10) in (6), we get

$$\int_0^\infty e^{-pt} y dt = \frac{C_0}{p} + \frac{C_1}{p-p_1} + \frac{C_2}{p-p_2} + \frac{C_3}{p-p_3} + \dots + \frac{C_n}{p-p_n} \dots \dots \dots (11)$$

On the other hand, the development of $\frac{1}{pH(p)}$ in partial fractions is well known to yield

$$\frac{1}{pH(p)} = \frac{1}{pH(0)} + \frac{1}{(p-p_1)p_1 H'(p_1)} + \frac{1}{(p-p_2)p_2 H'(p_2)} + \dots \dots \dots (12)$$

where

$$H'(p_m) = \left(\frac{dH}{dp} \right)_{p=p_m}.$$

Identifying again corresponding terms in (11) and (12), we find

$$C_0 = \frac{1}{H(0)}, \quad C_1 = \frac{1}{p_1 H'(p_1)}, \quad \dots, \quad C_n = \frac{1}{p_n H'(p_n)};$$

and thus we find :—

or, after grouping together the terms relating to each initial condition,

$$\begin{aligned} H(p) \int_0^\infty e^{-pt} y \, dt \\ = \frac{1}{p} + y(0) [a_0 p^{n-1} + a_1 p^{n-2} + a_2 p^{n-3} + \dots + a_{n-1}] \\ + y^{(1)}(0) [a_0 p^{n-2} + a_1 p^{n-3} + \dots + a_{n-2}] \\ + y^{(2)}(0) [a_0 p^{n-3} + \dots + a_{n-3}] \\ \dots \dots \dots \\ + y^{(n-1)}(0) a_0, \end{aligned}$$

which expression can be written as

$$\begin{aligned} H(p) \int_0^\infty e^{-pt} y \, dt = \frac{1}{p} + y(0) \left[\frac{H(p)}{p} \right] + y^{(1)}(0) \left[\frac{H(p)}{p^2} \right] \\ + y^{(2)}(0) \left[\frac{H(p)}{p^3} \right] + \dots + y^{(n-1)}(0) \left[\frac{H(p)}{p^n} \right], \\ \dots \dots (15) \end{aligned}$$

where by $\left[\frac{H(p)}{p^m} \right]$ is meant *that* part only of $\frac{H(p)}{p^m}$ which contains positive powers of p , the zero'th power included, the rest being omitted.

In the same symbolic way in which (9) was expressed we now obtain from (15)

$$\begin{aligned} \frac{y}{p} = \frac{1}{pH(p)} + y(0) \frac{1}{H(p)} \left[\frac{H(p)}{p} \right] \\ + y^{(1)}(0) \frac{1}{H(p)} \left[\frac{H(p)}{p^2} \right] + \dots + y^{(n-1)}(0) \frac{1}{H(p)} \left[\frac{H(p)}{p^n} \right]. \\ \dots \dots (16) \end{aligned}$$

When, in the same way as in the former problem, this expression (16) is written as a power series in p^{-1} , and thereupon the symbolic solution thus obtained is "algebrized" (which is Heaviside's expression, meaning the replacement of p^{-m} by $t^m/m!$), we obtain the solution of our problem.

The form of (16) clearly shows the individual effects of each of the initial conditions. With

$$y(0) = y^{(1)}(0) = y^{(2)}(0) = \dots = y^{(n-1)}(0) = 0,$$

Further, it will be obvious that

$$\int_0^{\infty} e^{-pt} [f(t)] dt = \int_0^{\infty} e^{-pt} f(t) dt,$$

as was the case with the "unity" function of the first problem.

The solution of any one of the Y 's in (14) is

$$Y_r = \frac{\Delta_r}{\Delta} \int_0^{\infty} e^{-pt} f(t) dt, \quad . \quad . \quad . \quad (19)$$

where Δ is the complete determinant of the system, and Δ_r its minor with respect to the r th term in the last row. Dropping the suffix r , we write this result

$$Y = \int_0^{\infty} e^{-pt} y(t) dt = \frac{F(p)}{\Delta(p)} \int_0^{\infty} e^{-pt} f(t) dt, \quad . \quad (20)$$

so that the integral equation (of Laplace type) for the unknown $y(t)$ is

$$\int_0^{\infty} e^{-pt} \left\{ y(t) - \frac{F(p)}{\Delta(p)} f(t) \right\} dt = 0, \quad . \quad . \quad (21)$$

where $f(t)$ is the force applied at the instant $t=0$, and where, from the nature of the problem, in which a stable system is assumed, the denominator has no roots with positive real parts, so that the Hurwitz conditions for $\Delta(p)$ are fulfilled. (20) or (21) are of the same form as (6), so that the two operational solutions given before can here again be applied to solve for y either as a series expansion in t or as a sum of characteristic vibrations. Moreover, if the initial values of the various differential coefficients are different from zero, it is possible to express the solution of the system in the same way as we did for a single equation. Thus the general problem of the behaviour of an invariable system, starting from any given initial conditions and acted upon by a force given as a function of the time, is found to be solvable by the aid of the above extension of Heaviside's operational calculus.

CXXXI. *Certain Molecular Lengths measured by an Optical Lever.* By W. N. BOND, M.A., D.Sc., F.Inst.P., *Lecturer in Physics in the University of Reading* *.

CONTENTS.

Summary.
Preliminary Experiments.
Apparatus used.
Experimental Results.
Analysis of the Results for Periodicity.
Evidence that the Periodicities are not Spurious.
Theories of the Action at the Contacts.

SUMMARY.

THE development, construction, and use of optical levers is described that enable certain single changes in the thickness of a sheet of mica to be measured to an accuracy of about 1.5×10^{-8} cm. On tilting the lever and letting it return gently on to the mica, apparent changes in thickness are observed. These changes are analysed for periodicity. The periodicity found with muscovite mica,

$$(10.0 \pm 0.3) \cdot 10^{-8} \text{ cm.},$$

is concluded to correspond to the length of the unit cell of muscovite, 9.95×10^{-8} cm. (as deduced from X-ray experiments). Steel, similarly, yielded a periodicity of

$$(6.8 \pm 0.2) \cdot 10^{-8} \text{ cm.},$$

which is attributed to the length of the cementite unit cell, 6.737×10^{-8} cm. (according to X-ray measurements).

It is shown that, in *each* of the four experiments described, so marked a periodicity so close to a possible X-ray value would only occur spuriously once in about 100 such experiments.

The results seem best explained by assuming that the needle-tip of the lever ruptures a certain number of the surface-layers of the crystal, these layers flowing radially outwards till the needle reposes on the first intact layer. If flow did not occur, it is estimated that pressures of from 30,000 to 180,000 atmospheres would have occurred at the contact. It is found necessary to conclude that a more or less ordered return flow of a small number of the surface-layers occurs when the needle-tip is withdrawn. This return flow is

* Communicated by the Author.

attributed to surface-tension or cohesion forces. Some experiments using selenite gave no evidence of any corresponding periodicity. This may have been due to the plastic nature of selenite, or to some experimental error.

Preliminary Experiments.

ABOUT three years ago an optical lever was constructed having an effective length of 1.3 mm., the legs consisting of three small ball-bearings soldered into the base of a piece of brass. The two outer legs rested in a slot and hole in the flat top of a brass block, the central leg resting on a flat on the block (or, later, on a ball-bearing fastened in the block). To facilitate a lever of such a small effective length remaining in stable equilibrium, a thin rubber band was arranged to pull the lever on to its support, the resultant force passing through the very flat isosceles triangle formed by straight lines joining the tips of the three legs.

This lever, when used with a lamp and scale at a metre distance, easily gave readings of the thickness of sheets of mica, or repeated zero settings, to an accuracy of 10^{-5} cm. As only quite rough usage moved the zero by more than that amount, it was decided to try to improve on the apparatus. The possibility was at that time considered of measuring the effective length of a mica molecular or unit cell by determining the thickness of a mica sheet at various points.

The designs of various types of measuring machine were considered, and considerable time was spent in attempting to form double levers of various forms that had geometrical constraints. These levers were, however, not very successful.

It seemed possible to improve the sensitivity of a single optical lever by obtaining a setting accurate to within a fraction of the width of the central diffraction band in the image of an illuminated slit. Early in 1928 I found a paper by Dr. C. V. Burton* showing that it was possible to take readings to very considerably less than the half-width of the central diffraction band, and work on these lines was commenced. The use of optical interference was thought inadvisable, as it does not easily lend itself to the measurement of other than gradual movements, and might necessitate the use of a heavy lever. For reasons of complication Prof. Whiddington's ultra-micrometer was also avoided. The

* Phil. Mag., March 1912, p. 385.

single optical lever has the advantage that all the measurements required are three lengths.

In the first of these experiments the lever of effective length 1.3 mm. was used. The return beam of light formed an image of a fine illuminated slit at a point effectively 50 cm. from the mirror, and this image was viewed with a Hilger travelling microscope (reading to 1/100 mm. and to 1/1000 mm. by estimation). Following Dr. Burton's method, accurate setting was obtained by almost eclipsing the central diffraction band in the image by a wire in the eyepiece of the microscope. In every case several settings of the microscope were made in succession between successive tiltings of the lever. The results showed considerable accuracy. For instance, without using any mica the lever was tilted and allowed to return to zero five times, and between these tiltings sets of microscope settings were made. Averaging each group of microscope settings, it was found that successive mean readings did not differ by more than about 10^{-7} cm.

A flake of mica was then placed between the central leg of the lever and the fixed steel ball on which it had previously rested. On tilting the lever and letting it return, larger changes in reading were obtained than when the mica was not present, and these were at that time attributed to lateral shifting of the mica having occurred when the lever was tilted. The observational error was, however, still rather too large to tell whether the changes between one reading and the next did or did not correspond to small integral multiples of the length of the mica unit cell.

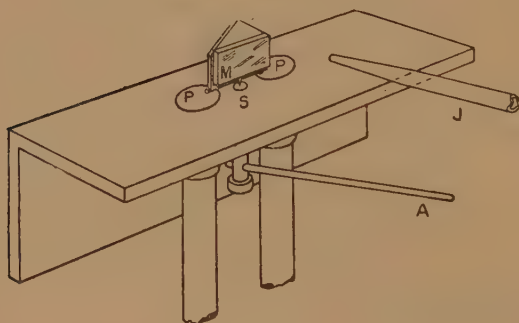
Apparatus used.

Since the results with the improved optical arrangement had been nearly accurate enough to give definite evidence for or against the possibility of detecting the molecular spacing by this means, it was decided to attempt to obtain about a ten-fold increase in sensitivity. As 1/1000 mm. seemed as small as it was convenient to measure accurately at the last stage of the system, it was decided not to follow Dr. Burton's method of actuating the micrometer screw by another screw, but to increase the optical path three-fold and decrease the length of the lever to a third or less. (The latter, if it were possible, would also decrease the relative effect of external disturbances.) To overcome the difficulty of obtaining stability of such a short lever, it was decided to use a steel lever the outer legs of which rested on the poles of a horse-shoe magnet. The centre of gravity of the lever

could then be at any reasonable distance from the vertical plane through the outer legs, provided it were on the same side of this plane as the central leg.

The optical lever.—Each lever used consisted of a short length of “hack-saw” blade L (fig. 1) about 1 cm. by 1 cm., at each end of the lower edge of which a $1/32$ inch diameter steel ball-bearing was soldered. At the centre of the lower edge either a third ball-bearing or the tip of a fine needle was soldered, not quite in line with the outer ball-bearings. (The imaginary plane touching the lower surface of the three legs must be as nearly perpendicular to the plane of the lever itself as possible.) To one face of the steel blade a thin mirror M (4 mm. by 9 mm.) was fastened with soft wax.

Fig. 1.

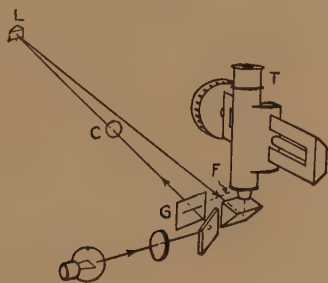


The support for the lever.—Two cobalt-steel $3/8$ -inch diameter bar magnets were fitted at the top with steel pole-caps PP (fig. 1) and joined by an iron yoke at the bottom. The steel pole-caps were soldered into holes in one face of a stout brass “angle-piece,” and half-way between the pole-caps the end of a hardened steel screw S came approximately flush with the top of the brass plate. The brass and pole-caps were polished flush and reasonably plane, and the tip of the central steel screw was made slightly convex so that any thin mica sheet pressed into contact with it by the central leg of the lever would not be constrained by the screw tip except close to the one point of contact. The central screw could be turned by means of a “tommy-bar” A to adjust the optical lever till the plane of the mirror was vertical. The magnetic attraction between the outer legs of the lever and the magnet pole-caps on which they rest prevents sliding

of the lever, even when the lever is intentionally tilted (unless the tilting is roughly performed). A hole-and-slot constraint in the pole-caps was not used, as it would increase the friction unduly.

The general arrangement of the apparatus.—The arrangement of the apparatus is illustrated in fig. 2. Light from one filament of an 8-volt "galvanometer lamp," passed through the convex lens in the lamp-fitting, was reflected from a mirror and passed through a fine slit G produced by ruling with a needle a fine line through the silvering of a glass mirror. The light then passed through an achromatic convex lens C (of about 33 cm. focal length) to the optical lever L. The return beam of light passed just to one side of C and produced an image of the slit G at a point F. The light was then reflected by a right-angled prism and

Fig. 2.



passed into the travelling microscope T, which was adjusted to view the image at F. (After preliminary adjustment, all the apparatus was kept fixed with the exception of the lever L and the microscope T.)

It was found convenient and satisfactory not to obtain accurate setting of the microscope by eclipsing the central diffraction band by a wire in the microscope eyepiece, but by setting a spider thread in the eyepiece centrally along the band.

Apparatus to tilt the lever.—In the present experiments the tilting of the lever was performed from a distance. In most cases a rubber bulb held in the hand was used to produce a small blast of air through the jet J (fig. 1) which tilted the lever by an amount that could be fairly controlled. In a few cases a copper wire moved by an electromagnetic relay was used to produce the tilting.

Experimental Results.

In the first experiments performed with this apparatus (a brief account of which was given in a letter to 'Nature' *), the tilting of the lever was performed by means of the tip of a pencil held in the hand. Dummy experiments showed that a correction for a general drift of the readings was necessary. This trouble was largely overcome in the subsequent experiments by tilting the lever without approaching it, as described in the previous section of this paper. This, and the increased rapidity with which the experiments could be performed, reduced any error due to drift. No drift or other correction was applied to any of the measurements given in the present paper.

The central leg of the lever could be arranged to rest on the tip of the steel screw S (fig. 1), or a loose flake of mica could be interposed, or the mica could be cemented down to the screw S with sealing-wax. In each set of experiments the lever was tilted so that its central leg no longer rested on S, and then the lever was allowed to descend again gently. A series of ten microscope settings on the image F (fig. 2) was then carried out, and the lever again tilted and the process repeated. The mean of each group of microscope settings was then calculated. These means may conveniently be designated "microscope readings." Consecutive microscope readings were then subtracted. This process of subtraction largely eliminates error due to a temporary or exponential drift that occurred just after descent of the lever.

These changes in the microscope reading, resulting from the tilting of the lever, were at first attributed to a lateral shifting of the mica (that was resting freely on the top of the screw S). It was however found that similar changes occurred even when the mica was cemented to S; and similar, though generally smaller, changes occurred when the leg of the lever rested directly on the screw S, without any mica between. The probable cause of these changes in microscope reading and the analysis of the changes for periodicity are considered later in the paper. It may be noted, however, that all the specially large changes were in the sense corresponding to a decrease in the thickness of the mica, but that the smaller changes corresponded more usually to an increase in the mica thickness.

In the present experiments the central leg of the levers consisted of the tip of a "No. 10" needle (in place of the

* 'Nature,' Aug. 4th, 1928, p. 169.

1/32-inch diameter steel ball previously used*). The effective length of the levers was measured directly by means of a travelling microscope. The details of the levers are given below :—

TABLE I.
Details of Optical Levers used.

Lever.	Nature of tip of central leg.	Radius of curvature of tip of leg.	Effective length of lever (cm.).	Mass of lever.
<i>a</i>	{ "No. 10" needle }	—	{ 0.0115 ± 0.0005 }	0.42 gm.
<i>b</i>	{ The same re-sharpened }	0.001 ₀ cm.	{ 0.0120 ± 0.0003 }	

The general properties of the mica used in these experiments are recorded in the following table:—

TABLE II.
Properties of the Mica used.

White and biaxal. Value of 2E compared with that for a specimen of muscovite:—

Present sample..... 26 $\frac{1}{2}$ } scale-divisions.
Specimen of muscovite..... 26 $\frac{1}{2}$ }

The principal refractive indices of the present specimen, for sodium light, were found:—

$$\alpha = 1.563_1$$

$$\beta = 1.593_6$$

$$\gamma = 1.598_9.$$

(These fall within the range given by muscovite.)

The measurements obtained in the lever experiments, using a flake of mica, are recorded in Tables III. and IV. The results of experiments in which no mica was used, the needle-tip of the lever resting directly on the steel screw S (fig. 1), are given in Tables V. and VI. The analysis of these results for periodicity and the meaning of the results are considered in the following sections of the paper.

* 'Nature,' *loc. cit.*

TABLE III.

Mica experiments (mica resting freely on screw S, fig. 1).

Lever length: $0.011,5 \pm 0.000,5$ cm.Distance LF (fig. 2): 161.8 ± 0.1 cm.Differences between consecutive microscope readings (each reading being the mean of 10 settings) in 10^{-4} cm.(+ corresponds to an increased *descent* of the lever.)

+ 1.2	+ 60.5
+ 94.0	+ 30.6
- 80.0	- 0.3
+ 3.5	- 3.9
+ 7.9	+ 184.1
- 164.3	- 2.3
+ 143.6	+ 35.6
+ 25.7	+ 28.2
+ 54.0	+ 36.4
	+ 169.9
	- 94.7
	+ 81.8

TABLE IV.

Mica experiments (mica cemented to screw S, fig. 1).

Lever length: $0.012,0 \pm 0.000,3$ cm.Distance LF (fig. 2): 114.9 ± 0.1 cm.Differences between consecutive microscope readings (each reading being the mean of 10 settings) in 10^{-4} cm.(+ corresponds to an increased *descent* of the lever.)

- 72.8	- 32.0
- 4.4	- 1.5
+ 474.2	- 129.8
- 110.2	- 112.4
- 22.6	+ 23.0
+ 476.2	+ 1006.9
- 166.3	- 109.0
- 0.7	- 48.6
+ 219.3	
- 155.9	
+ 279.5	

TABLE V.

Steel experiments.

Lever length : $0.011,5 \pm 0.000,5$ cm.Distance LF (fig. 2) : 115.5 ± 0.1 cm.Difference between consecutive microscope readings (each reading being the mean of 10 settings) in 10^{-4} cm.(+ corresponds to an increased *descent* of the lever.)

- 7.6	+10.0
-10.3	+14.9
-21.7	-37.1
-27.8	-13.4
-11.2	-28.4
-60.8	+25.4
- 0.2	-14.6
-28.3	-12.6
-23.3	+52.8

TABLE VI.

Steel experiments.

Lever length : $0.012,0 \pm 0.000,3$ cm.Distance LF (fig. 2) : 115.2 ± 0.1 cm.Difference between consecutive microscope readings (each reading being the mean of 10 settings) in 10^{-4} cm.(+ corresponds to an increased *descent* of the lever.)

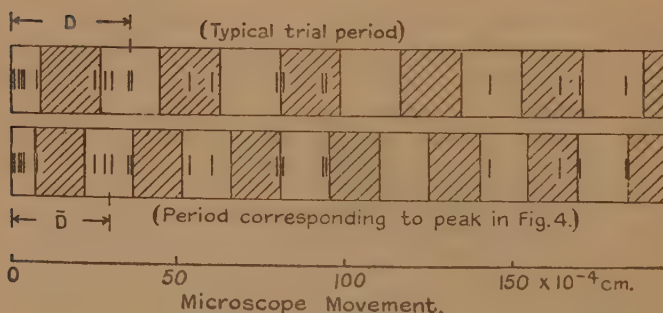
-15.9	- 25.2
+ 1.8	-214.2
-24.1	+119.9
-23.7	- 18.9
+25.9	+204.8
-14.6	- 26.0
-34.7	+ 0.7
-15.1	+607.5
+17.9	- 15.7
-29.4	\pm 0.0
-12.7	

Analysis of the Results for Periodicity.

If the differences between consecutive microscope readings contained any periodicity due to the mica (or steel) consisting of an array of unit or molecular cells such as is revealed by X-ray analysis, the periodicity would probably not be of sine form, but would consist of a series of isolated peaks separated by distances that are various integral multiples of some presumed "unit length." Experimental errors would have the effect of broadening the peaks, and for their detection it is necessary that the average experimental error shall be appreciably less than an amount corresponding to half the "unit length."

The most suitable test for such a periodicity, which gives equal "weight" to each observation, and which does not

Fig. 3.



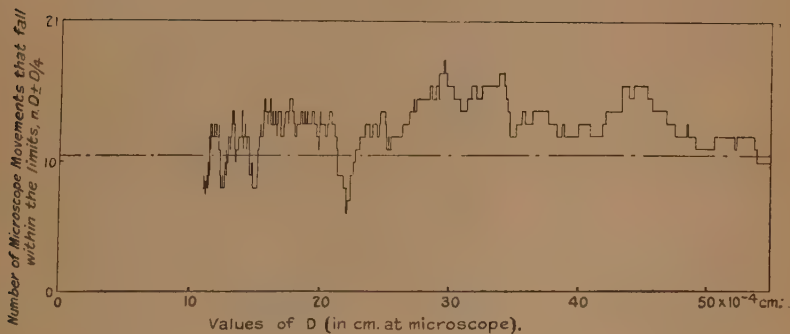
involve excessive calculation, consists in assuming in turn various trial values D for the "unit length" and finding what number of observations fall nearer to integral multiples of the "unit length" than to the intermediate odd multiples of the half "unit length" (indicated in fig. 3 by their falling in the unshaded rather than the shaded spaces). The result of such an analysis of the measurements recorded in Table III. is shown graphically in fig. 4*.

* The peak may be made to appear considerably more prominent by plotting as ordinates not the number of observations falling in the "unshaded" parts, but, for instance, the *ratio* of this number of observations to the number falling in the "shaded" parts (see *Phil. Mag.* 1. p. 640, 1925).

A well-defined peak is observed in the curve (fig. 4) with apex at $\bar{D} = 29.45 \times 10^{-4}$ cm. (at microscope), corresponding to about 10×10^{-8} cm. at the mica. (The best estimate of the value does not usually coincide exactly with the apex of the curve.) This periodicity is concluded to represent one due to the mica varying in thickness in some way by whole numbers of mica unit cells. The evidence for this peak not being a fortuitous one is given in the following section of the paper.

In fig. 3 the 21 changes in microscope reading given in Table III. are shown to scale, all being termed positive for convenience. The length \bar{D} corresponds to the trial "unit

Fig. 4.



length" that fits the results most successfully. For that trial "unit length" 18 of the 21 observations differ from

integral multiples of the value of D by less than $\pm \frac{D}{4}$. The

probability of any one at all of the 21 being more than $\frac{D}{2}$

in error is thus certainly less than 0.2. We may assume, therefore, that each observation corresponds to the integral multiple of \bar{D} nearest to it. We may also assume that the changes of reading corresponding to a movement of zero molecular or unit cells should be zero, and hence neglect the 6 readings close to zero. Collecting in tabular form, we get:

TABLE VII.

Changes in mica thickness. (From Table III.)

Number of molecular or unit cells increase.	Microscope change (in 10^{-4} cm.).	Deduced best estimate.	Residuals v .
+6	164.3	175.0	-10.7
+3	94.7 80.0	87.5	+ 7.2 - 7.5
0	$\begin{pmatrix} 3.9 \\ 2.3 \\ 0.3 \\ 1.2 \\ 3.5 \\ 7.9 \end{pmatrix}$	0	+ 3.9 + 2.3 + 0.3 - 1.2 - 3.5 - 7.9
-1	25.7 28.2 30.6 35.6 36.4	29.2	+ 3.5 + 1.0 - 1.4 - 6.4 - 7.2
-2	54.0 60.5	58.3	+ 4.3 - 2.2
-3	81.8 94.0	87.5	+ 5.7 - 6.5
-5	143.6	145.8	+ 2.2
-6	169.9 184.1	175.0	+ 5.1 - 9.1

Sum = 1283.4

 $\Sigma |v| = 99.1$ $1283.4/44 = 29.17$

Hence :—

Probable error value of the deviation of a single change
in microscope reading from the best estimate

$$= \pm 0.845 \frac{99.1}{\sqrt{21.20}} \times 10^{-4} \text{ cm.} = \pm 4.1 \times 10^{-4} \text{ cm.}$$

Mean value of microscope change for the length of one
unit cell of mica

$$= \frac{1283.4 \pm 4.1 \sqrt{15}}{44} \times 10^{-4} \text{ cm.} = (29.17 \pm 0.36) \times 10^{-4} \text{ cm.}$$

Estimated length of unit cell of mica (see Table III.)

$$= \frac{(29.1_7 \pm 0.36) \cdot 10^{-4} \text{ cm.} \times (0.001,5 \pm 0.000,5) \text{ cm.}}{2 \times (161.8 \pm 0.1) \text{ cm.}}$$

$$= (10.3_5 \pm 0.5) \times 10^{-8} \text{ cm.}$$

Very similar calculations were made with the measurements contained in Tables IV., V., and VI. The four sets of results are collected in Table VIII. (Some measurements made using selenite did not give any evidence of a corresponding periodicity. This may have been due to the plastic nature of selenite or to some experimental error.)

TABLE VIII.

Nature of contact.	Lever length. (cm.)	Distance from lever to microscope (LF fig. 2). (cm.)	Peak of curve.		Deduced estimate of unit cell length.		
			Height.	Microscope movement. (cm.)	Microscope movement. (cm.)	Cell length. (cm.)	Mean. (cm.)
Steel-mica	0.011,5	161.8	18 in 21	$10^{-4} \times$	$10^{-4} \times$	$10^{-8} \times$	$10^{-8} \times$
	$\pm 0.000,5$	± 0.1		29.4_5	$\begin{Bmatrix} 29.1_7 \\ \pm 0.4 \end{Bmatrix}$	$\begin{Bmatrix} 10.3_5 \\ \pm 0.5 \end{Bmatrix}$	$\begin{Bmatrix} 10.0 \\ \pm 0.3 \end{Bmatrix}$
	0.012,0	114.9	16 in 19	18.9	$\begin{Bmatrix} 18.8 \\ \pm 0.1 \end{Bmatrix}$	$\begin{Bmatrix} 9.8 \\ \pm 0.3 \end{Bmatrix}$	$\begin{Bmatrix} 10.0 \\ \pm 0.3 \end{Bmatrix}$
	$\pm 0.000,3$	± 0.1					
Steel-steel	0.011,5	115.5	16 in 18	12.7	$\begin{Bmatrix} 12.8 \\ \pm 0.2 \end{Bmatrix}$	$\begin{Bmatrix} 6.4 \\ \pm 0.3 \end{Bmatrix}$	$\begin{Bmatrix} 6.8 \\ \pm 0.2 \end{Bmatrix}$
	$\pm 0.000,5$	± 0.1	18 in 21	13.5	$\begin{Bmatrix} 13.5 \\ \pm 0.1 \end{Bmatrix}$	$\begin{Bmatrix} 7.0 \\ \pm 0.2 \end{Bmatrix}$	$\begin{Bmatrix} 6.8 \\ \pm 0.2 \end{Bmatrix}$
	0.012,0	115.2					
	$\pm 0.000,3$	± 0.1					

In the case of the muscovite mica the periodicity found in a direction perpendicular to the cleavage

$$(10.0 \pm 0.3) \cdot 10^{-8} \text{ cm.,}$$

clearly corresponds to the distance between cleavage planes as obtained by X-ray analysis *,

$$9.95 \times 10^{-8} \text{ cm.}$$

The two estimates of the periodicity given in Table VIII. differ from this value by less than their probable errors.

The experiments with steel give a periodicity of

$$(6.8 \pm 0.2) \cdot 10^{-8} \text{ cm.,}$$

* C. Mauguin, *Comptes Rendus*, p. 288, July 25th, 1927.

and this would be presumed to correspond to some unit cell length, or distance between cleavage planes. Three types of crystal have been found by X-ray methods, any of which might be concerned. These are:—

α , β , and δ ferrite * (body-centred cubic), sides of unit cell

$$2.87 \cdot 10^{-8} \text{ cm.},$$

γ ferrite † (face-centred cubic), sides of unit cell

$$\left. \begin{array}{l} 3.601 \\ \text{to } 3.629 \end{array} \right\} 10^{-8} \text{ cm.},$$

cementite ‡ (Fe_3C) (orthorhombic), sides of unit cell

$$4.518 \times 10^{-8} \text{ cm.}$$

$$5.069 \quad , \quad ,$$

$$6.737 \quad , \quad ,$$

Of these three crystals, the spacing of the first two would in any case not be observable in the present experiments, being so small that it would be just fully masked by experimental error. The observed spacing is definitely in best agreement with the long length of the cementite unit cell. We must therefore assume cementite present at the surface of the needle-tip, of the screw S (fig. 1), or of both. It must be further assumed that the cementite close to the surface was orientated so that the length of the orthorhombic unit cells was at right angles to the surface of the steel. This is in accord with what is found in the case of many crystals, and with what is found for thin layers of chain-compounds when forming a surface film on water.

The observed values of periodicity $(6.4 \pm 0.3) \cdot 10^{-8} \text{ cm.}$ and $(7.0 \pm 0.2) \cdot 10^{-8} \text{ cm.}$, both differ from the length of the cementite cell, $6.737 \cdot 10^{-8} \text{ cm.}$, by slightly more than the probable errors, but fall on opposite sides of it in value.

We will now consider the evidence that the periodicities found are not spurious due to fortuitous circumstances; and also discuss theories as to the reason for the periodicity being observable in the optical lever experiments.

* Heindlhofer, *Phys. Rev.* xxiv. pp. 426-438, Oct. 1924.

† Westgren and Phragmén, 'Nature,' cxiii. pp. 122-124, January 26th, 1924.

‡ Westgren and Phragmén, *Journal Iron and Steel Inst.* cix. pp. 159-172, 1924. (See also *Internat. Crit. Tables*, i. pp. 340, 349, and references.)

Evidence that the Periodicities found are not spurious.

Magnitude of the experimental errors.—It is best first to show that the accuracy of measurement was great enough to permit the detection of the periodicities.

The average accuracy of any single setting of the travelling microscope T (fig. 2) on the image F can be deduced (irrespective of any extra error due to a steady or gradually changing drift) by calculating in a number of cases the difference between any single setting and the mean of the ones immediately preceding and following it. The probable error value of these differences can be shown to be $\sqrt{3/2}$ times the probable error of a single setting.

TABLE IX.

Experiments.	Error of single microscope setting.	Error of single difference between consecutive microscope readings (each reading being the mean of ten settings).			
		Estimated by grouping the microscope settings in sets of five.		Deduced by comparison with best estimate of $n \cdot \bar{D}$.	
		at microscope.	at lever.	at microscope.	at lever.
	$\times 10^{-4}$ cm.	$\times 10^{-4}$ cm.	$\times 10^{-8}$ cm.	$\times 10^{-4}$ cm.	$\times 10^{-8}$ cm.
Steel- { mica {	± 2.9 ± 3.3	± 2.8 ± 2.8	± 1.0 ± 1.5	± 4.1 ± 3.4	± 1.5 ± 1.8
Steel- { steel {	± 1.8 ± 2.7	± 1.5 ± 2.0	± 0.7 ± 1.0	± 1.8 ± 1.9	± 0.9 ± 1.0

The accuracy of the differences between successive microscope readings (each reading being the mean of ten settings) can be fairly estimated by comparing the results obtained by using only the first five settings in each group with the results obtained using only the last five settings in each group. This may somewhat underestimate any error due to a drift if it is present.

For comparison, the probable error value may be found of the deviation of any difference between successive microscope readings from the nearest integral multiple of the best estimate of the periodicity "unit length." (A set of these residuals was given in the last column of Table VII., and below was given the probable error value.)

These three estimates of error are summarized in Table IX., for the four sets of experiments.

It will be seen that the predicted errors (column 4) are on the whole slightly less than those apparently found (last column). Hence the personal errors of microscope setting, together with any small amount of general drift of readings, was not so large as to be likely to mask periodicities of the magnitude of those apparently detected. (The predicted errors are, as mentioned above, probably slightly underestimated.)

The small probability of obtaining spurious periodicities so well marked as those observed, and the small probability of such spurious periodicities so close to the expected values.—It will be convenient to consider the first set of measurements (Tables III. and VII.) to illustrate the method of calculation. Let us assume the points in fig. 3 to be distributed at random, instead of as observed. For any value of D chosen at random (except excessively large values) the chance of any one point falling within the limits $n \cdot D \pm D/4$, where n is an integer, is $1/2$. The chance (for any fixed value of D) of 18 or more out of 21 points falling within the above limits is

$$\frac{{}^{21}C_0 + {}^{21}C_1 + {}^{21}C_2 + {}^{21}C_3}{2^{21}} = \frac{1}{1340} \text{ (approximately).}$$

(18 out of 21 observations fell between the above limits when $D = 29.4_5 \times 10^{-4}$ cm. at microscope—see fig. 3 and Table VIII.)

Now, when $D = \infty$, all the points fall within $\pm D/4$ of zero. As D is decreased steadily, a fresh arrangement of the 21 points in the compartments shown in fig. 3 occurs each time either boundary of any compartment passes any point. Each such transition is shown as a step in a graph such as fig. 4. Over any small range of the graph these transitions are independent, being due to different points (that were assumed distributed at random). Over a larger range the transitions are not strictly independent, but are sensibly so. Hence, usually about 1340 steps in the graph fig. 4 should contain (1 ± 1) peaks as high as 18 in 21 or higher. Now, the number of transitions between the observed peak and infinity is only 87 in the present instance. Hence, such a peak is not to be expected fortuitously anywhere between the observed position and infinity, its probability being only about $87/1340$.

If we further assume the length of the mica unit cell as obtained by X-ray measurements* (9.95×10^{-8} cm.), we can

* C. Mauguin, *loc. cit.*

deduce the corresponding value of D in centimetres of microscope movement (limited by the probable errors of measurement of the optical lever length, and of the distance LF , fig. 2). The value so deduced in the present instance $(28.0 \pm 1.2) \cdot 10^{-4}$ cm. at the microscope, falls 7 transitions away from the peak of the curve (fig. 4). The chance of obtaining a spurious peak of height (18 or more in 21) within 7 independent transitions of the expected place, when normally about 1340 such independent transitions would be required, is only $7/1340$.

Similar calculations have been made for the other three sets of observations, and are collected together (Table X.).

In the case of the steel-steel experiments the X-ray value of the length of the cementite unit cell has been used as the "expected value." No periodicity was expected when

TABLE X.

Experiment.	Height of peak in periodicity curve.	Number of random trials to obtain such a peak.	Actual number of trials between the peak and ∞ .	Probability of such a peak fortuitously between the peak position and ∞ .	Number of trials between the peak and the expected value.	Probability of such a peak fortuitously so near to the expected place.
Steel- mica }	18 in 21	1340	87	0.065	7	0.005
	16 in 19	452	363	0.80	4	0.009
Steel- steel }	16 in 18	1522	62	0.041	4	0.003
	18 in 21	1340	215	0.16	8†	0.006

† In this case the 8 are not independent, four being due to the largest reading (Table VI.). If this reading be omitted, however, the probability 0.006 is not measurably changed.

the experiments were made; but since only three spacings suggested by X-ray measurements are large enough to have been detectable, the order of magnitude of the probability will not be much changed.

It will be seen that in three of the four cases such a peak would not have been expected as a result of fortuitous circumstances; and in all four cases its nearness to a value suggested by X-ray data cannot be attributed to chance.

Theories of the Action at the Contacts.

Three theories of the action at the contact have been considered. The detection of a periodicity might be attri-

buted to a lateral movement of the mica (or the lever) during the tilting of the lever; or to an interpenetration of the crystal lattices of the two bodies between which contact is made; or to flow of one or both solids near the point of contact.

It was found that periodicity occurred even when the mica was fixed; and it occurred when the needle rested on the fixed steel below. By viewing the lever with a microscope it was found certainly not to move laterally by more than 0.005 mm. in the course of a dozen tiltings. To see what this implies it is necessary to estimate the area of contact at the needle-tip. The area of contact may be estimated by the calculations due to Hertz (though they are not strictly applicable to a sphere resting on a plane, nor unless both the bodies are isotropic). The radius of the circle of contact will be of the order

$$\sqrt[3]{\frac{3}{4} \left(\Sigma \frac{1-\sigma^2}{E} \right) \cdot r \cdot P},$$

where r is the radius of curvature of the tip of the needle, σ and E are Poisson's ratio and Young's modulus for the materials, and P is the total static force. Since the mass of the lever was about 0.42 gram, and the centre of gravity was 0.5 mm. in front of the vertical plane through the outer legs (owing to a small projecting weight not shown in fig. 1), the static force at the contact is about 1700 dynes.

Taking $r = 0.001$ cm. (see Table I.) and $\Sigma \frac{1-\sigma^2}{E}$ as about 2.5×10^{-12} cm.²/dyne, we get the radius of the "circle" of contact to be of the order 0.0015 mm. Since a dozen tiltings did not produce any lateral movement as great as twice the estimated diameter of the circle of contact, it follows that lateral movement cannot be causing the thickness of the mica to be measured each time at an effectively different place; and hence such movement cannot account for the observed periodicity.

The second hypothesis (the interpenetration of the crystal lattices of the two bodies) would predict that the apparent change in thickness on tilting the lever, when it rested on mica, might be the sum or difference of integral multiples of the unit cell lengths of steel and mica. If this were so, the smaller steel periodicity would quite mask that due to the mica and prevent its detection. Hence this hypothesis also must be abandoned.

For the third hypothesis, that of flow of the solid near the point of contact, it is necessary to show that the pressure due to the lever may be large enough to produce movement.

Again following Hertz, the pressure at the centre of the circle of contact may be shown to be of the order

$$\frac{3}{2\pi} \left(\frac{4}{3r \Sigma \frac{1-\sigma^2}{E}} \right)^{2/3} \times P^{1/3}.$$

Hence, for the lever resting on mica, the pressure (if no flow took place) would reach the order 33,000 atmospheres. For the maximum possible free fall of the lever (0.0013 cm. at the needle-tip), the value might reach 80,000 atmospheres. And for steel on steel 180,000 atmospheres might be attained when such impact occurred. These estimated pressures appear to be as large as the likely values of the intrinsic pressures in mica and steel; and hence flow may be considered possible.

When steel rests on steel a flow of one or both is postulated. And when mica is interposed, it is assumed that the mica will flow and not the steel. This is likely, as it is well known that steel will easily scratch mica without being itself noticeably affected. The steel periodicity would thus not mask any due to the mica.

It is known that flow or slip takes place most readily parallel to a cleavage plane. And hence, when the needle impinges on the steel or mica we may postulate that a certain number of the surface layers of mica or steel are penetrated and then move fairly freely outwards parallel to the surface. The first layer not penetrated will then be bent by the needle reposing on it, and the area of contact must become so large that the pressure nowhere exceeds that required to cause penetration of the layer. The first layer not penetrated would thus settle the depth to which the needle descended; and, consequently, successive positions would differ by integral multiples of the unit cell length of the material below the needle (or of the material of the needle, if that were the more easily penetrated).

It is further necessary to explain why small *increases* in thickness are observed, that also show the unit cell periodicity. We may assume that when the needle is withdrawn, and the intense local pressure removed, surface tension or cohesion forces cause a return flow of the surface layers previously penetrated by the needle. This closing up (or partial closing)

of a small pit in the surface may be compared with the aggregation of more or less isolated parts of thin metal films as found by Beilby*. In the case of the metal films the temperature had been raised somewhat, and the effect was probably not very rapid. However, in the present case the maximum increase found is only of the order of ten molecular or unit cells ; and on the removal of the intense local pressure this amount of return flow is not at all inconceivable.

In one respect the flow must differ from what Sir George Beilby considered took place on polishing a crystal surface †. It must here be assumed that the return flow takes place in layers that retain their thickness more or less unaltered, and do not become quite amorphous as Beilby supposed in his experiments.

Beilby, however, shows that subsequent crystallization of an isomorphous crystal on the polished surface took place with an orientation settled by the original crystal (unless the disturbed layer between were specially thick). And though he attributed this to action at a distance through the amorphous layer, it is conceivable that the layer is not perfectly amorphous. It might retain its layer formation approximately ; and in the present experiments the radial surface flow is probably more ordered than when polishing is performed by hand.

In conclusion, I should like to thank Prof. J. A. Crowther, in whose laboratory the work was carried out, for permitting and even encouraging what might be considered at least a speculative piece of research to undertake. To Prof. A. W. Porter my best thanks are due for his criticism and advice, which have contributed considerably to the completion of the work.

University of Reading,
Department of Physics,
December 31st, 1928.

* Proc. Roy. Soc. A, lxxii. pp. 232-3.

† *Op. cit.* lxxxii. p. 599.

CXXXII. *A Comparison of Whitehead's with Einstein's Law of Gravitation.* By WILLIAM BAND, B.Sc., George Holt Physics Laboratory, The University of Liverpool*.

1. Foreword.

IN a communication entitled "General Orbits in Relativity Dynamics by the Hamiltonian Method" (Phil. Mag. No. 284, pp. 277-292), G. Temple has shown that the dynamic invariants given by Einstein and Whitehead give precisely the same form to the equations of planetary orbits. His work, however, rests on the assumed distinctions between the metric and dynamic invariants ds and dJ respectively. If we follow Einstein and identify ds with dJ , then we find that Temple's Lagrange equations reduce to the identity $0=0$. In this case we must therefore examine Whitehead's invariant by the usual geodesic method, calculating the three-index symbols for the particular values of the fundamental tensor that he uses.

2. Whitehead's First Expression.

This can be written

$$\begin{aligned} ds^2 &= (1-2m/r)dt^2 - (1+2m/r)dr^2 \\ &\quad \pm 4m/r \cdot dr dt - r^2 d\theta^2 - r^2 \sin^2 \theta d\phi^2 \\ &= g_{\mu\nu} dx_\mu dx_\nu, \end{aligned}$$

where the indices refer to (r, θ, ϕ, t) taken in order, and where the unit of time is $3 \cdot 10^{-10}$ second.

We then have

$$\begin{aligned} -g_{11} &= 1 + 2m/r \\ -g_{22} &= r^2, & -g_{33} &= r^2 \sin^2 \theta \\ g_{14} &= g_{41} = 2m/r \\ g_{44} &= 1 - 2m/r \end{aligned}$$

giving by the usual definition

$$\begin{aligned} -g^{11} &= 1 - 2m/r \\ -g^{22} &= r^{-2}, & -g^{33} &= r^{-2} \sin^{-2} \theta \\ -g^{14} &= -g^{41} = 2m/r \\ g^{44} &= 1 + 2m/r. \end{aligned}$$

* Communicated by Prof. J. Rice, M.A.

Evaluating the three-index symbols defined by

$$[\mu\nu, \lambda] = \frac{1}{2} [\partial g_{\mu\lambda} / \partial x_\nu + \partial g_{\nu\lambda} / \partial x_\mu - \partial g_{\mu\nu} / \partial x_\lambda]$$

$$\{\mu\nu, \lambda\} = g^{\lambda\sigma} [\mu\nu, \sigma],$$

we find, when we neglect powers of r lower than -2 ,

$[11, 1] = -m/r^2$	$\{11, 1\} = -m/r^2$
$[11, 4] = -2m/r^2$	$\{11, 4\} = -2m/r^2$
$[22, 1] = r$	$\{22, 1\} = -r(1-2m/r)$
	$\{22, 4\} = -2m$
$[33, 1] = r \sin \theta$	$\{33, 1\} = -r \sin \theta (1-2m/r)$
	$\{33, 4\} = -2m \sin^2 \theta$
$[33, 2] = r^2 \sin \theta \cos \theta$	$\{33, 2\} = -\sin \theta \cos \theta$
$[44, 1] = -m/r^2$	$\{44, 1\} = m/r^2$
	$\{44, 4\} = \text{negligible}$
$[21, 2] = [12, 2] = -r$	$\{21, 2\} = \{12, 2\} = 1/r$
$[31, 3] = [13, 3] = -r \sin \theta$	$\{31, 3\} = \{13, 3\} = 1/r$
$[41, 4] = [14, 4] = m/r^2$	$\{41, 4\} = \{14, 4\} = m/r^2$
$[23, 3] = [32, 3] = -r^2 \sin \theta \cos \theta$	$\{23, 3\} = \{32, 3\} = \cot \theta$
	$\{14, 1\} = \{41, 1\} = \text{negligible}.$

We now obtain the geodesics defined by

$$d^2 x_\alpha / ds^2 + \{\mu\nu, \alpha\} dx_\mu / ds \cdot dx_\nu / ds = 0, \quad (1)$$

giving for the various values of α :—

$$1. \quad d^2 r / ds^2 - mr^{-2} (dr/ds)^2 - r(1-2m/r) (d\theta/ds)^2 - r^2 \sin^2 \theta (1-2m/r) (d\phi/ds)^2 + m/r^2 (dt/ds)^2 = 0. \quad (2)$$

$$2. \quad d^2 \theta / ds^2 + 2/r \cdot (dr/ds) (d\theta/ds) - \sin \theta \cos \theta (d\phi/ds)^2 = 0. \quad (3)$$

$$3. \quad d^2 \phi / ds^2 + 2/r \cdot (dr/ds) (d\phi/ds) + 2 \cot \theta (d\theta/ds) (d\phi/ds) = 0. \quad (4)$$

$$4. \quad d^2 t / ds^2 - mr^{-2} (dr/ds)^2 - 2m (d\theta/ds)^2 - 2m \sin^2 \theta (d\phi/ds)^2 + 2m/r^2 \cdot (dr/ds) (dt/ds) = 0. \quad (5)$$

If we arrange for θ to be zero, (3) shows that it remains zero, allowing us to write (4) and (5) in the simpler forms :

$$d^2 \phi / ds^2 + 2/r \cdot (dr/ds) (d\phi/ds) = 0. \quad (4')$$

$$d^2 t / ds^2 + 2m/r^2 (dr/ds) (dt/ds) = 2m \{1 - r^{-2} (dr/d\phi)^2\} (d\phi/ds)^2. \quad (5')$$

Equation (4') gives, as usual,

$$d\phi/ds = h/r^2. \quad (6)$$

Equation (6) shows that in (5') the right-hand side may be equated approximately to zero, giving the usual solution

$$dt/ds = c(1 + 2m/r). \quad . \quad . \quad . \quad . \quad (7)$$

Putting θ zero in the expression for ds^2 , we get

$$ds^2 = (1 - 2m/r)dt^2 - 4m/r \cdot dr dt - (1 + 2m/r)dr^2 - r^2 d\phi^2. \quad (8)$$

Then by (6), (7), dividing through (8) by ds^2 , we get

$$(1 + 2m/r)(dr/d\phi)^2 (d\phi/ds)^2 = (1 - 2m/r)(dt/ds)^2 \\ - r^2 (d\phi/ds)^2 - 4m/r (dr/d\phi)(d\phi/ds)(dt/ds) - 1,$$

giving

$$(r^{-2} dr/d\phi)^2 = (1 - 4m/r)(1 + 4m/r)c^2/h^2 \\ - (1 - 2m/r)/h^2 - (1 - 2m/r)/r^2 \\ - 4m/r(1 - 2m/r)(c^2/r^2)(1 + 2m/r)(1/h)dr/d\phi$$

or

$$\left[\frac{1}{r^2} dr/d\phi \right]^2 = (c^2 - 1)/h^2 + 2m/h^2 r \\ - 1/r^2 + 2m/r^3 - (4mc/hr^2)dr/d\phi. \quad . \quad . \quad (9)$$

The equation corresponding to (9) arising from Einstein's expression for ds^2 is identical therewith, save for the term in $dr/d\phi$, which is there absent.

Now, if we are to neglect this term, we must confine our applications to motions in which the eccentricity of the orbit is small, for in other cases, *e.g.* motions of the comets, Whitehead's expression will no longer give correct results.

3. Whitehead's Second Expression.

Following Temple, we can write this:

$$ds^2 = (1 - 2m/r)dt^2 - 2F(r)dr dt \\ - dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta d\phi^2, \quad . \quad . \quad (1)$$

where $F(r)$ is a function of r only, tending to zero as r approaches infinity. We then have

$$-g_{11} = 1 \\ -g_{22} = r^2, \quad -g_{33} = r^2 \sin^2 \theta \\ -g_{14} = -g_{41} = F(r) \\ g_{44} = 1 - 2m/r,$$

and since

$$-g^{11} = g_{44} [g_{14}^2 - g_{11}g_{44}]^{-1} \\ g^{14} = g^{41} = -g^{11}g_{14}/g_{44} \\ g^{44} = g^{11}g_{11}/g_{44},$$

we get, putting

$$\begin{aligned} R &\equiv [F(r)^2 + 1 - 2m/r] \doteq 1, \quad . \quad . \quad (2) \\ -g^{11} &= (1 - 2m/r) R^{-1}, \quad g^{44} = 1/R \\ -g^{22} &= r^{-2}, \quad -g^{33} = r^{-2} \sin^2 \theta \\ -g^{14} &= -g^{41} = F(r) R^{-1}. \end{aligned}$$

From these the three-index symbols become

$$\begin{aligned} \{11, 1\} &= 0 & \{44, 1\} &= m(1 - 2m/r)/Rr^2 \\ \{11, 4\} &= -F'(r) \cdot R^{-1} & \{44, 4\} &= mF(r)/Rr^2 \\ \{22, 1\} &= -r(1 - 2m/r)R^{-1} & \{41, 4\} &= \{14, 4\} = m/Rr^2 \\ \{22, 4\} &= -rF(r)R^{-1} \\ \{33, 1\} &= -r \sin^2 \theta (1 - 2m/r)R^{-1} & \{33, 4\} &= -r \sin^2 \theta F(r) \cdot R^{-1}, \end{aligned}$$

where the dash denotes differentiation with respect to r .

The rest remain as for the first expression (see § 2, above).

The geodesics for $\alpha=2, 3$ are precisely as before, giving, when θ is zero, the solution (6) of § 2.

The geodesic for α equals 4, then becomes, as a first approximation, the solution 2 (7).

The orbit is again obtained from the interval, giving

$$\begin{aligned} [1/r^2 \cdot dr/d\phi]^2 &= (c^2 - 1)/h^2 - 1/r^2 + 2mc^2/h^2r \\ &\quad - 2F \cdot (c^2/h)(1 + 2m/r)(1/r^2 \cdot dr/d\phi). \quad . \quad (3). \end{aligned}$$

If in this we neglect the term in $dr/d\phi$, the orbit reduces to a Newtonian form.

Temple obtained the value

$$F(r) = c\sqrt{2m/r}.$$

Putting this in (3), and remembering that for planetary motion h is of the order r , we see that even were we to retain the term in question, the correction involved therein is negligible in comparison with Einstein's correction to Newton. There appears to be no further significance to Temple's value for $F(r)$.

4. Conclusions.

It appears that Whitehead's first dJ^2 is only approximate, and that his second is not even that, unless, as he assumes, the metric is independent of the gravitation field. Temple, however, having shown that the Einstein dS^2 is satisfactory even on this last assumption, it has the double advantage of simplicity and independence of the particular theoretical interpretation.

CXXXIII. *The Motion of a Particle as a Statistical Problem and Bohr-Heisenberg's Uncertainty Conditions.* By D. MEKSYN*.

1. *Rigorous and Statistical Laws.*

THE laws of Physics are usually classified in two distinct groups: the rigorous laws of microscopic, and the statistical laws of macroscopic phenomena. The two classes of laws are quite different in their character. There can be no exception to rigorous laws; on the other hand, statistical laws give us only the probable course of a phenomenon. A body in a gravitational field must always move according to the same law; even a single exception would completely overturn the particular theory of gravitation adopted; on the other hand, statistical laws admit exceptions: heat may sometimes flow from a cold body to a hot one, this would not make the second law of Thermodynamics invalid.

The difference between these two classes of laws does not lie, however, in this particular point: we have practically just as little chance of observing heat flowing from a cold body to a hot one, as of seeing a body moving against the law of gravitation; the observed deviations from the second law are only confined to microscopic regions. What seems to be more important is the origin of these two categories of laws.

The rigorous laws of microscopic phenomena are considered to be laws of Nature; they do not depend upon the skill of the observer. Different is the origin of statistical laws; they are not prescribed laws of Nature, but are intimately connected with our nature and means of observation.

Two conditions are necessary in order that a statistical law may exist: (1) the particular system must be limited in such a way that every possible state of it shall have, although a small, yet a finite probability; (2) our means of observation must be such that we are able to measure only average values of quantities.

The development of Physics for the last twenty years, mainly in the theory of Radiation, has thrown some doubts on the validity of this classification.

As it is known, the line spectrum of a substance is due to jumping of electrons from one stable orbit into another; the intensity of such radiation is proportional to the number of atoms in which such changes take place, this number being

* Communicated by the Author.

governed by laws of probability. Hence the intensity of radiation is a purely statistical phenomenon. On the other hand, according to Bohr's Principle of Correspondence, the same intensity can be found, at least to the first approximation, from classical electrodynamics, based on rigorous laws of motion.

The case just mentioned may be a mere coincidence, which will be explained when we possess a rigorous theory of radiation, or perhaps the difficulty lies deeper in that the distinction between the laws is wrong.

2. *The Origin of Physical Laws.*

It may be that every microscopic phenomenon is governed by rigorous laws of Nature, and that a complex, or macroscopic phenomenon, is governed by statistical laws, which are substitute laws, which arise either because we do not yet know the microscopic law, or because our means of observation are too rough to follow each constituent separately (as in the theory of gases).

The other view is that microscopic laws do not exist, the behaviour of each constituent is possibly arbitrary (within certain limits), and is governed by laws of probability; the observed laws of Nature are then influenced by the limitation of our means of observation.

If we meet a regularity in Nature it is because we observe either the average state of many systems, or of a single system during a relatively long interval of space and time.

We shall investigate the second point of view, and consider that the laws of Dynamics are only statistical laws.

DYNAMICS OF A MATERIAL POINT.

3. *Probability as the Basis of Laws of Motion.*

To find the laws of motion we must bear in mind the following consideration: in order that statistical laws may exist, every possible state must possess, if a small, yet a finite probability, and physical conditions must be regarded as imposing some limitations upon probabilities.

In the case of motion this means that the material point in a free space or in a field of force will be enclosed with great probability within a narrow cylindrical portion of the space, or in order that statistical laws of motion may exist there must be in space tracks of greatest probability.

We assume for the probability that an electron will describe some arbitrary track s' and not the track of greatest

probability s (s' and s have the same ends) the well-known expression for the probability of errors

$$dW = Ce^{-\frac{(s'-s)^2}{\lambda^2}} d(s'-s). \quad (1)$$

If s is a geodesic line, the limits of $\Delta s = s' - s$ are 0 and ∞ .

4. The Law of Motion.

From (1) it follows that the greatest probability will have the track for which

$$\Delta s = 0. \quad (2)$$

At first sight (2) appears to be a mere repetition of the assumption that a track, s , exists which has the maximum probability.

But we may allow the equation (2) to define the track of greatest probability, and so suppose that we have to find s where

$$\Delta s = 0.$$

This equation is satisfied in so far as terms of the first order are concerned along a geodesic where

$$\delta s = 0. \quad (3)$$

We come thus to the Law of Motion in the General Principle of Relativity.

Let us find the track, that will be observed. The coefficient C in (1) is found from

$$C \int_0^\infty e^{-\frac{x^2}{\lambda^2}} dx = 1$$

or $C = \frac{2}{\lambda \sqrt{\pi}},$

and the average value of Δs in

$$\bar{\Delta s} = \frac{2}{\lambda \sqrt{\pi}} \int_0^\infty x e^{-\frac{x^2}{\lambda^2}} dx = \frac{\lambda}{\sqrt{\pi}}. \quad (4)$$

The equation (1) could also be interpreted as follows: the greatest probability is that for which ΔS is a small quantity; for a geodesic line the variations $\delta x, \delta y$, which make ΔS small, will have the greatest values. Or the particle has the greatest probability of motion in those parts, of space, where it can move with the greatest freedom.

We may say that the particle moves in geodesic regions. This permits of comparatively great variation of position and velocity. From equation (8), which follows later, it is easily

seen that, for the hydrogen atom, these variations are of the same order of magnitude as the quantities themselves.

In order to complete the solution of our problem and obtain the actual form of the geodesic line, we must know the form of the phase space.

In two cases, at least, there is a definite solution, and this is for a uniform rectilinear motion, and for gravitation.

Several suggestions have been made as to the form of space in the case of the existence of an electromagnetic field. Kaluza, Klein, and others have suggested a five dimensional space, and in a recent paper* I have shown that, in the case of n electrons, a $4n$ dimensional space leads also to a geodesic motion.

5. Limit of Exactness of Measurements.

We have to fix λ . The dimension of $\frac{s}{c}$ is time, therefore $\frac{\lambda}{c}$ must be of the same dimension. We assume for $\frac{\lambda}{c}$ the period of de Broglie's wave associated with an electron or

$$\frac{\lambda}{c} = \frac{h}{mc^2} \cdot \cdot \cdot \cdot \cdot \cdot (5)$$

This assumption, together with (4), leads us at once to Heisenberg's conditions for exactness of measurements.

From (4) and (5) we have

$$\overline{\Delta s} \sim \frac{h}{mc} \cdot \cdot \cdot \cdot \cdot \cdot (5a)$$

For a geodesic line the first variation of s vanishes, and in order to find the meaning of (5a) we have to evaluate the second variation of s . We could, however, also make use of the first variation, if only we carry out the integration not along a geodesic, but along a somewhat deformed line, whose first variation is equal to $\frac{\lambda}{\sqrt{\pi}}$.

We consider the case of a uniform rectilinear motion.

We have

$$\begin{aligned} \delta s &= \delta \int_{t_1}^{t_2} (c^2 \dot{t}^2 - \dot{x}^2 - \dot{y}^2 - \dot{z}^2)^{\frac{1}{2}} dt \\ &= \int_{t_1}^{t_2} \left\{ \frac{d}{dt} \left(\frac{\dot{x}}{\sqrt{c^2 - u^2}} \right) \cdot \delta x + \frac{d}{dt} \left(\frac{\dot{y}}{\sqrt{c^2 - u^2}} \right) \cdot \delta y \right. \\ &\quad \left. + \frac{d}{dt} \left(\frac{\dot{z}}{\sqrt{c^2 - u^2}} \right) \cdot \delta z - \frac{d}{dt} \left(\frac{c^2}{\sqrt{c^2 - u^2}} \right) \cdot \delta t \right\} dt \quad (6) \end{aligned}$$

* Phil. Mag. 1928, p. 977.

or from (5a) and (6), since $\delta x, \delta y, \delta z, \delta t$ are independent displacements, we obtain :

$$\left. \begin{aligned} & \left| mc \int_{t_1}^{t_2} \frac{d}{dt} \left(\frac{\dot{x}}{\sqrt{c^2 - \dot{x}^2}} \right) \delta x \cdot dt \right| \sim h, \\ & \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\ & \left| mc \int_{t_1}^{t_2} \frac{d}{dt} \left(\frac{c^2}{\sqrt{c^2 - \dot{x}^2}} \right) \delta t \cdot dt \right| \sim h. \end{aligned} \right\} \dots \dots (7)$$

These equations could be also written, as $(t_2 - t_1)$ is small, as follows :—

$$\left. \begin{aligned} & \overline{\delta p \cdot \delta q} \sim h, \\ & \quad \vdots \quad \vdots \quad \vdots \quad \vdots \\ & \overline{\delta E \cdot \delta t} \sim h, \end{aligned} \right\} \dots \dots \dots (8)$$

where q, p, E denote the coordinates, momenta, and energy of an electron. These are Heisenberg's conditions.

The same equation (8) could also be obtained from the second variation from our geodesic line.

We have

$$\begin{aligned} \Delta S &= \frac{1}{2} \int_{t_1}^{t_2} \left(\frac{\partial^2 F}{\partial \dot{x}^2} \delta \dot{x}^2 + 2 \frac{\partial^2 F}{\partial \dot{x} \partial \dot{y}} \delta \dot{x} \delta \dot{y} + \dots \right) dt, \\ &\sim \frac{h}{mc} \quad \text{on the average,} \end{aligned}$$

where $F = (c^2 \dot{t}^2 - \dot{x}^2 - \dot{y}^2 - \dot{z}^2)^{\frac{1}{2}}$.

For a velocity much less than c , we have

$$\frac{\partial^2 F}{\partial \dot{x}^2} \simeq \frac{1}{c},$$

hence $\int_{t_1}^{t_2} \delta \dot{x}^2 dt \sim \frac{h}{m}$

or $m(\delta \dot{x})^2 \Delta t \sim h. \dots \dots (9)$

Now $\left. \begin{aligned} m \delta \dot{x} &= \delta p, \\ \delta \dot{x} \Delta t &= \delta(\dot{x} \Delta t) = \delta q, \end{aligned} \right\} \dots \dots (10)$

and from (9) and (10) we again obtain the first equation of (8).

In a recent paper Dr. H. T. Flint has suggested a different meaning for the conditions (1)*. It appears from some metrical considerations that the world line of an electron can

* Roy. Soc. Proc. cxvii. p. 630.

be considered as made up of integral multiples of a fundamental length $s = \frac{h}{mc}$ (the velocity of light $t = 1$), and Dr. Flint has suggested that nothing less than this fundamental length could be directly or indirectly observed. The considerations developed in this paper provide a somewhat different explanation of this suggestion.

In conclusion, we recapitulate the main ideas of this paper.

A particle does not possess a definite track, but moves in regions of greatest probability, hence all elements of motion are merely statistical quantities.

Laws of Physics can give us only the limitations upon probabilities. This is, for instance, the meaning of Schrödinger's Equation. This function provides us with a quantity for the measurement of the greatest probability of state. It does, however, not follow that an electron is forced to remain indefinitely in such a state. Given sufficient time it may deviate to such an extent from this position that it will come to another one of maximum probability. This is the cause of spontaneous radiation of an atom.

I wish to express my thanks to Dr. N. T. Flint for much useful criticism and assistance in the writing of this paper.

Added to the Proof.—We have assumed in (1) that the probability depends upon the length of a world track; this appears rather arbitrary. This assumption can, however, easily be connected with Schrödinger's Equation in relativistic form.

The approximate solution of this equation for a quasi-stationary motion is

$$\text{const. } e^{\frac{2\pi i}{h}\phi} \phi = \int_{t_0}^t \rho_1 dx_1 + \rho_2 dx_2 + \rho_3 dx_3 - (\nu + \rho_4 c) dt,$$

where $\rho_1 \dots \rho_4$ is the momentum energy vector, and ν is the potential of the external field.

Now ϕ can be transformed in

$$\phi = - \int_{t_0}^t \left(mc^2 \sqrt{1 - \frac{v^2}{c^2}} + \nu \right) dt,$$

which is the usual Hamiltonian, and (3) becomes $\delta\phi = 0$.

Wheatstone Laboratory,
King's College, London.
May 1st, 1929.

CXXXIV. *On Prof. R. D. Kleeman's Derivation of the Law of Mass Action.* By RICHARD F. GOLDSTEIN, Ph.D.*

IN the January number of the *Philosophical Magazine*† there appeared a letter by the present author, drawing attention to some errors invalidating the conclusions of an earlier paper of Prof. R. D. Kleeman‡, in which he sought to disprove the classical Law of Mass Action.

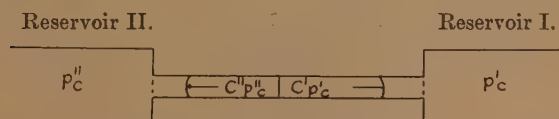
In reply §, Prof. Kleeman reiterated his original statements and invited the writer to develop his arguments further. He therefore takes this opportunity of doing so.

To follow Prof. Kleeman's nomenclature, in the reaction :—



the molecules C, D are so-called "seprounstable," and on removal from the equilibrium box, dissociate spontaneously into their equilibrium mixtures. From this new standpoint, Prof. Kleeman developed his ideas.

For the sake of simplicity, consider first the species C.



c mols of C at pressure p_c'' are removed from reservoir II. and immediately dissociate into their equilibrium mixture a pressure $C''p_c''$ still keeping the partial pressure of C at p_c'' . According to Prof. Kleeman, the free energy change associated with this removal is nil. But since the dissociation of seprounstable molecules of C is a spontaneous process, it follows from the Second Law of Thermodynamics that the change must be associated with a diminution in free energy. Indeed, if the diminution in free energy in the spontaneous decomposition is zero, it necessarily follows that the change in free energy in the recombination of the decomposition mixture to pure C is also zero. To take a concrete example, if this were so, CO_2 at 900°C. would decompose into its equilibrium mixture of CO_2 , CO and O_2 containing 25 per cent. CO_2 with no diminution in free

* Communicated by the Author.

† *Phil. Mag.* (7) vii. p. 205 (1929).

‡ *Ibid.* v. p. 263 (1928).

§ *Ibid.* vii. p. 206 (1929).

energy, and we could recombine the gaseous mixture to CO_2 without the expenditure of any work.

By removing the c mols of C from reservoir II. at pressure p''_c to a third reservoir, and then allowing C to decompose into its equilibrium mixture at pressure $C'p''_c$, the chief error in Prof. Kleeman's argument may be demonstrated even more clearly, since the spontaneous decomposition of C at pressure p''_c to give the gaseous equilibrium mixture at a higher pressure $C'p''_c$ may be made to do useful work, for example, by expansion against a constant pressure. The decomposition of the seprounstable molecules under isothermal reversible conditions must therefore be associated with a diminution in free energy, even allowing for the maintenance of the partial pressure of the seprounstable molecules at a constant value, and whether we obtain the decomposition products in two stages or in one.

On the return of the decomposition products of C at pressure $C'p''_c$ to reservoir I. as c mols of C at pressure p'_c , Prof. Kleeman has similarly and erroneously assumed that the recombination of the decomposition products to C takes place with no change in free energy. Since the decomposition and recombination of C take place at different pressures, the two equilibria are, in general, different and the two changes in free energy are not equivalent. Prof. Kleeman's main argument is therefore disproved.

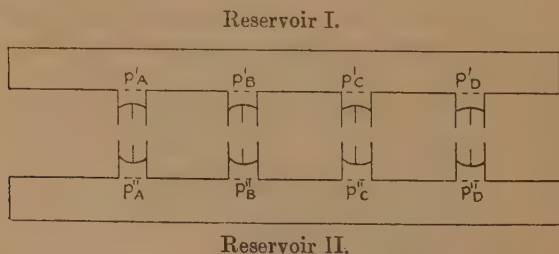
In like manner, the same arguments apply to the procedure adopted by Prof. Kleeman for the transference of d mols of D from reservoir II. at pressure p''_d to reservoir I. at pressure p'_d .

That van't Hoff's derivation of the Law of Mass Action is not invalidated by the concept of seprounstable molecules may be demonstrated by the following reasoning:—

In the change



A, B being seprostable and C, D seprounstable



it is agreed that in the transference of a mols of A and b mols of B from reservoir I. to II. under isothermal, reversible conditions, the increase of free energy :

$$\Delta F_A + \Delta F_B = aRT \ln \frac{p''_A}{p'_A} + bRT \ln \frac{p''_B}{p'_B}.$$

For the transference of c mols of C and d mols of D from reservoir II. to I. under isothermal reversible conditions we have choice of several routes, along any of which the increase of free energy must be the same, since this depends solely on the initial and final states of the systems and not on the route chosen.

For example, we have among others the following options:—

(1) We can compress C and D from pressures p''_c, p''_d to p'_c, p'_d , without allowing any spontaneous decomposition to take place (for example, by carrying out the transference in infinitesimal time, or supposing the velocity of decomposition to be extremely small).

(2) We can remove C and D from reservoir II. at pressures p''_c, p''_d , allow them to decompose to the equilibrium mixtures at pressures $C''p''_c, D''p''_d$, recombine to C and D at pressures p''_c, p''_d , compress to pressures p'_c, p'_d and introduce into reservoir I.

(3) We can follow Prof. Kleeman's route, by removing C and D from reservoir II., allowing to decompose to mixtures at pressures $C''p''_c, D''p''_d$, compressing the mixtures to pressures $C'p'_c, D'p'_d$ (at which C and D have partial pressures p'_c, p'_d) recombining to C and D at pressures p'_c, p'_d , and introducing into reservoir I.

Whatever route we follow, the increment of free energy in the change of c mols of C and d mols of D from pressures p''_c, p''_d to pressures p'_c, p'_d must be the same. And the increase in free energy in either routes (1) or (2) is obviously

$$\Delta F_C + \Delta F_D = cRT \ln \frac{p'_c}{p''_c} + dRT \ln \frac{p'_d}{p''_d}.$$

Since the net change in free energy in the whole process is zero,

$$\Delta F_A + \Delta F_B + \Delta F_C + \Delta F_D = 0$$

$$\text{or } aRT \ln \frac{p''_A}{p'_A} + bRT \ln \frac{p''_B}{p'_B} + cRT \ln \frac{p'_c}{p''_c} + dRT \ln \frac{p'_d}{p''_d} = 0 \quad \dots \quad (1)$$

which leads by simple rearrangement to the classical van't Hoff equation.

It should be pointed out that the change in free energy in transferring the seprounstable molecules C and D from reservoir II. to reservoir I. by Prof. Kleeman's route cannot be calculated directly without assuming the Law of Mass Action, but recourse has to be had to alternative methods.

In his latest communication on this subject*, Prof. Kleeman endeavours to substantiate his conclusions by calculation of the work done instead of the free energy increments in the transference of the seprounstable molecules C and D from reservoir II. to I. by his route.

He states that equation (1) then assumes the form :

$$RT \ln \frac{(p''_c)^c (p''_d)^d}{(p''_a)^a (p''_b)^b} + RT \ln \frac{(p'_c)^c (p'_d)^d}{(p'_a)^a (p'_b)^b} + X$$

where X is, in general, a finite quantity.

It should be sufficient to point out that if this is so, the the First Law of Thermodynamics is violated since a suitable cycle could be constructed which would produce useful work for an indefinite period.

Prof. Kleeman's kinetic derivation of his new law is equally fallacious.

In the equation

$$K = \frac{K_1 k_1}{K_2 k_2},$$

k_1 , k_2 express the chances of molecules encountering, and are a measure of the number of collisions taking place per unit time. Prof. Kleeman introduces two "activation" factors, K_1 , K_2 which control the number of *effective* collisions that take place. That is to say, if in the reaction



the number of collisions of a molecule A with another molecule A is k_1 , the number of collisions leading to formation of B is $K_1 k_1$, where K_1 is, in general, a number less than unity.

Now Prof. Kleeman goes on to say †, " But the quantities K_1 , K_2 , evidently depend on the frequencies of the encounters and on their nature, and are therefore functions of the fundamental independent variables, the volume of the mixture, its temperature, and the masses of the elemental constituents."

* Phil. Mag. (7) vii. p. 206 (1929).

† *Ibid.* v. p. 271 (1928).

A more rigid proof than mere assertion would be welcome. The K 's are ratios of effective collisions to total collisions, *i. e.*, derivatives of activity coefficients.

The writer must also take exception to Prof. Kleeman's equations (11) and (12) in his first paper *.

For the reaction :



he writes :

$$K_1 k_1 C^2_{\text{CO}_2} = K_2 k_2 C^2_{\text{CO}} C_{\text{O}_2}, \quad . \quad . \quad . \quad (11)$$

whence he says

$$K = \frac{K_1 k_1}{K_2 k_2}, \quad . \quad . \quad . \quad (12)$$

but this implies that

$$K = \frac{C^2_{\text{CO}} C_{\text{O}_2}}{C^2_{\text{CO}_2}},$$

the equation he has been endeavouring to show is incorrect ! Finally, in his reply † to the writer, Prof. Kleeman in addition has been confusing activities with activity coefficients.

In the reaction, which he cites



the constant of mass action

$$K = \frac{(A_{ce})^2}{A_{c_2} A_{e_2}} = \frac{(\alpha_{ce} C_{ce})^2}{[\alpha_{c_2} C_{c_2}] [\alpha_{e_2} C_{e_2}]}, \quad . \quad . \quad . \quad (2)$$

where the A 's are *activities* and the α 's *activity coefficients*.

From (2),

$$K = \frac{(\alpha^2_{ce})}{\alpha_{c_2} \alpha_{e_2}} \times \frac{C^2_{ce}}{C_{c_2} C_{e_2}},$$

which is of the same form as

$$K = \frac{K_1}{K_2} \times \frac{k_1}{k_2},$$

since k_1, k_2 represent the velocities of collision dependent on the concentration, and K_1, K_2 , control the effectiveness of the collisions.

That is to say, K_1, K_2 , are simple derivatives of the activity coefficients of the reagents.

* Phil. Mag. (7) v. p. 271 (1928).

† Ibid. vii. p. 207 (1929).

CXXXV. *Notices respecting New Books.*

Revision of Rowland's Preliminary Table of Solar Spectrum Wave-lengths, with an Extension to the Recent Limit of the Infra-red.
By CHARLES E. ST. JOHN, CHARLOTTE E. MOORE, LOUISE M. WARE, EDWARD F. ADAMS, and HAROLD D. BABCOCK. [Pp. xxi+238.] (Carnegie Institution of Washington: Publication No. 396. Papers of the Mount Wilson Observatory, Vol. III. 1928.)

THE publication of the revision of Rowland's solar wave-lengths has been eagerly awaited by spectroscopists. The investigations upon which it is based have been carried on at the Mount Wilson Observatory for more than a decade. The method of revision is summarized in the Introduction to the volume as follows:—

“The results rest upon two independent series of measurements; in each a large number of lines, well distributed and sufficiently isolated to serve for standards, have been measured. One series depends upon simultaneous exposures to the centre of the Sun and the standard iron arc with the 30-foot spectrograph and the 60-foot tower telescope in the earlier period, and with the 75-foot spectrograph and the 150-foot tower telescope in the later period. The other series was made with the interferometer, used at first with the spectrograph of the Snow telescope on Mount Wilson for the accessory dispersion, and later with the laboratory installation in Pasadena.

“The two series, corrected for the rotation and orbital motion of the earth, are in excellent agreement; the differences for individual lines rarely exceed 0.002 \AA , while the systematic deviation is of the order of a few ten-thousandths of an angström. With the means of these two series as reference points, the wave-lengths of a still larger number of lines were interpolated upon spectrograms of high dispersion.”

It is found that Rowland's wave-lengths are remarkably consistent for short spectral regions, but that over extended regions the corrections vary in a curiously progressive way.

The main table contains the wave-length of each line in the International System; the identification; the intensity; the intensities of lines in sun-spot spectra relative to the intensities in the spectrum of the disk; the temperature classification from furnace spectra; the classification from the behaviour of the lines under pressure, in the explosive spark and in the high-current arc; the excitation potential of all lines whose multiplet designations are known.

For completeness the Mount Wilson measures of the infra-red region from $\lambda 7333$ to $\lambda 10218$ are given in a separate table with additional information analogous to that given in the main table.

Separate lists are given of the strongest unidentified solar

lines; of lines normally present in the chromosphere only; and of bright lines attributed to the corona. An additional table of great value contains the term designations for excitation potentials for the different atoms, including ionized atoms.

A list of 57 elements definitely identified in the Sun's atmosphere is given in the Introduction. Of the 35 elements not yet identified in the sun, 17 are regarded as possible and 18 as doubtfully possible of detection. Tables are given of the comparative representation of the elements and of the percentage of enhanced lines per element.

The volume reflects the highest credit upon the Mount Wilson Observatory and upon those who have collaborated in its production. It will prove of the greatest value to physicists and to astronomers.

The Collected Works of J. WILLARD GIBBS. Vol. I. *Thermodynamics*. [Pp. xxviii+434.] Vol. II. Part One. *Elementary Principles in Statistical Mechanics*. [Pp. xviii+207.] Part Two. *Dynamics; Vector Analysis and Multiple Algebra; Electromagnetic Theory of Light, &c.* [Pp. vi+284.] (New York and London: Longmans, Green and Co. 1928. Price 15s. each volume, or the two volumes 25s. net.)

THE former edition of Willard Gibbs's writings, published in 1906, has long been out of print. During the intervening years, there has been a greatly increased appreciation of the fundamental importance of his work, and, in particular, of his writings on the subjects of statistical mechanics and on the equilibrium of heterogeneous substances. The new reprint is therefore an event of importance, particularly as the volumes are offered at a price which should make them available to a wide circle of readers. This low published price has been made possible by the generosity of Professor Irving Fisher, of Yale University, a former pupil of Willard Gibbs, and by the employment of photographic methods of reproduction. The reproduction has been well done, and it is not easy to detect that the pages have not been printed from newly-set type.

The value of the present edition is increased by the inclusion of a reprint of Gibbs's treatise, "Elementary Principles in Statistical Mechanics." This was originally published as a separate book, and was not included in the former edition of the collected works. It has for some time been out of print. The present reprint is therefore the first complete edition of Gibbs's published writings.

The editors state that they have under consideration the publication, at a later date, of a commentary, written by recognized authorities in the several fields, designed to aid the student of Gibbs's writings. Such a volume would prove of undoubted value, and it is to be hoped that the project will be brought to fruition.

Modern Physics. By H. A. WILSON, M.A., D.Sc., F.R.S. [Pp. xiv+381.] (London: Blackie and Son. 1928. Price 30s. net.)

BASED on lectures given to students taking an Honours Course in physics, the volume contains a concise and up-to-date account of the present position of modern physics, suitable for advanced students. The subjects dealt with cover a wide range and are necessarily treated somewhat briefly. They include electron theory; theories of magnetism; thermionics; photoelectricity; quantum theory; the critical potentials of atoms; X-rays, cathode rays, α -, β -, and γ -rays; optical spectra; positive rays; radioactive transformations; constitution of atoms; gaseous ions; the motion of electrons in gases; the electrical conductivity of flames; the positive glow and negative glow; atmospheric electricity; special and general relativity and gravitation. At the end of each chapter, references are given to treatises on the subject-matter of the chapter, suitable for more advanced and specialized study.

A number of examples on the subject-matter of each chapter, to be worked by the student, are given at the end of the volume. In the mathematical sections, mathematical difficulties are carefully avoided; a chapter is devoted to vector operations in these dimensions, and the operations of tensor calculus are explained.

As an introduction to specialized study the volume can be thoroughly recommended.

The Conduction of Electricity through Gases. By Sir J. J. THOMSON, O.M., F.R.S., and G. P. THOMSON, M.A. Third Edition. Vol. I. [Pp. viii+491, with 121 figures.] (Cambridge: at the University Press. 1928. Price 25s. net.)

TWENTY-TWO years have elapsed since the publication of the second edition of Sir J. J. Thomson's well-known work on the conduction of electricity through gases. In the interval a vast number of researches on the subject have been published. The preparation of a new edition was commenced fifteen years ago, and the publication has at length become possible with the cooperation of Professor G. P. Thomson. Physicists will be grateful to the authors for having undertaken the very heavy task of summarizing the work that has been done since 1906.

It has been necessary to extend the book to two volumes. The volume under review covers the ground of the first ten chapters of the earlier edition, and deals with the general properties of the ions and with ionization by heat and light. Most of the original paragraphs have been retained with the original numbering; new paragraphs, dealing with subjects cognate to one of the original paragraphs, receive the same number, followed by a decimal. This procedure has the advantage of maintaining continuity with the earlier editions and of enabling the new material to be easily identified.

References to original papers are given throughout, and there are numerous diagrams of apparatus and experimental results. No physicist can afford to be without the authoritative account of an important branch of the subject.

The Nature of the Physical World. By A. S. EDDINGTON, M.A., LL.D., D.Sc., F.R.S. [Pp. ix+361.] (Cambridge: at the University Press. 1928. Price 12s. 6d. net.)

THE publication of the Gifford Lectures, delivered by Prof. Eddington in 1927, will make available to a wider circle a brilliant exposition of the nature of the physical world as viewed from the standpoint of modern science. The first portion of the book is devoted to the new scientific outlook. In Prof. Eddington's words: "The modern scientific theories have broken away from the common standpoint which identifies the real with the concrete." The new theories, which have brought about the downfall of classical physics,—relativity, the quantum theory, and wave-mechanics—are described; these chapters form a model of what popular scientific exposition should be—clear, accurate, and stimulating. The nature of the fundamental entities used in modern physics—length, mass, time, and so forth—is discussed at some length. The difference between the field laws of physics and the quantum laws is clearly elucidated: the former are shown to be mere truisms; the latter are regarded as laws of governance of the material universe.

The latter portion of the book is more speculative, dealing with what the author terms "the problem of relating these purely physical discoveries to the wider aspects and interests of our human nature." The application of what Prof. Eddington terms the "principle of indeterminacy of behaviour" to the question of "free-will" provides interesting reading and has far-reaching consequences. The question as to whether our knowledge is confined to what we can discover by scientific methods has an application to the mind.

The volume is a masterly exposition which provides fascinating reading both for the scientist and for the philosopher.

Non-Riemannian Geometry. By L. P. EISENHART, Professor of Mathematics, Princeton University. American Mathematical Society Colloquium Publications, Vol. VIII. [Pp. viii+184.] (New York: 1928. English Agents, Bowes and Bowes, Cambridge. Price \$2.50.)

THE recent developments of the theory of relativity have drawn attention to non-Riemannian geometry, and the appearance of this volume comes at an opportune time. The non-symmetric displacements which are at the basis of Einstein's latest theory are treated in the first chapter on asymmetric connexions, the projective geometry of paths, and the geometry of sub-spaces.

The volume is suitable for advanced mathematical students. Prof. Eisenhart's own contributions to the subject are considerable, and no better exposition of the mathematical theory could be desired. A full bibliography is appended and full references to it are given throughout the text. The volume forms an important addition to the valuable series of Colloquim Lectures published by the American Mathematical Society.

An Introduction to the Chemistry of Plant Products. Vol. I. *On the Nature and Significance of the Commoner Organic Components of Plants.* By P. HAAS, D.Sc., Ph.D., and T. G. HILL, D.Sc., A.R.C.S. Fourth Edition. [Pp. xvi+530.] (London: Longmans, Green and Co. 1928. Price 18s. net.)

THE fourth edition of Messrs. Haas and Hill's 'Chemistry of Plant Products' follows the same general lines as the third edition, when the work was divided into two volumes. The first volume deals mainly with the more chemical side of the subject—the occurrence and chemistry of the chief products of plant activity, such as fats, oils, waxes, aldehydes and alcohols, carbohydrates, glucosides, tannins, pigments, colloids, proteins, and enzymes. The more purely physiological problems are dealt with in the second volume.

The great increase in biochemical investigation during recent years has necessitated the inclusion of much additional matter, seven years having elapsed since the last edition appeared. The book has been thoroughly revised and to a large extent rewritten, and the volume under review contains 120 pages more than the previous edition.

The work is well annotated with references to original papers and has a detailed index. Both for study and reference the new edition will prove of great value to all engaged in biochemical work.

CXXXVI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 904.]

March 6th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

Mrs. M. M. OGILVIE GORDON, D.Sc., F.G.S., delivered a lecture on the Structure of the Western Dolomites.

She described briefly the stratigraphical succession of the Permian and Triassic rocks which mainly compose the mountain-lands of the Western Dolomites, and showed their character in a number of photographic slides. Special attention was given to

the outbreaks of volcanic action which took place in the Upper Buchenstein and Wengen periods at the close of the Alpine Middle Trias. These were associated with long crust-fissures in a west-north-westerly and east-south-easterly direction, in the course of which numerous vents occurred. Sills and dykes of andesite were much more frequent than had been supposed, although the sills were near the surface, and differed little from the lava-flows. Crust-movements took place, and certain areas were relatively uplifted as submarine terraces while inthrows occurred along the volcanic zones. Discordances and alternations were shown between the lavas and tuffs of the volcanic zones and the Marmolata Limestone or Schlern Dolomite that formed on the terraces.

Volcanic action continued in much lessened degree during the Cassian time, tuffs intermingling locally with the calcareous and marly deposits. The seas were shallower, and were marked out on the north of the tuff accumulations of Fassa into a number of protected basins. Growths of coral-limestone ('Cipit Limestone') were prevalent along the edges of the submarine terraces; they were frequently brecciated by surf action, and helped to extend the base upon which the limestone and dolomite of the terraces could form. Conditions, however, might vary, and the marly deposits and reef-limestones encroach upon the terrace-slopes.

Mojsisovic's presentation of the coral-reef origin of the great thicknesses of Schlern Dolomite was founded largely upon geological sections which showed the Wengen and Cassian strata banked up against steep walls of Schlern Dolomite, regarded as original reef-walls. But detailed observations over a wide area had shown a gradual passage of facies: for example, in Cassian time, from Cassian tuff-conglomerates, tuffs, and marls rich in fossils to lenticular reef-formations or blocks of Cipit Limestone, and from these to typical Schlern Dolomite. A number of photographs from the Fermeda group, Sella, Langkofl, and Schlern, demonstrated the passage of local alternations and facies. The facts pointed to algal formations as in great measure the origin of the Schlern Dolomite.

The next succeeding group of Raibl Sandstones and Marls also showed facies relations with the Schlern Dolomite. They had been deposited upon irregular surfaces of that dolomite, sometimes in shallow basin-shaped areas, sometimes on surfaces of abrasion. In the frequent unconformities, the upper layers of Raibl strata overstepped the lower. The group thus thinned, and passed into dolomitic facies in the direction in which the Schlern Dolomite swelled out in thickness.

An east-to-west section from the St. Cassian to the Ampezzo district showed the form of the Schlern Dolomite of that area, which in Lagazuoi Mountain was about 1600 feet thick, and thinned out gradually both towards east and west. Eastwards it thinned within 3 miles into the Cassian and Raibl strata of the Romerlo meadowland, westwards within $2\frac{1}{2}$ miles into the same groups on the west of Valparola Alpe.

The Dachstein Dolomite, which succeeds the Raibl strata, forms a massive deposit throughout the Enneberg and Ampezzo district, but has been mostly eroded from the western area.

The leading structural features were described, with the aid of the geological map of the Gröden and Fassa district published by the lecturer in 1927. Several phases of mountain-movement could be distinguished in this district. During the regional movements of uplift of the Eastern Alps the whole district had been thrown into anticlines and synclines extending almost due east and west (N. 80° – 85° W.). These were cut by numerous east-to-west vertical faults. Later, during periods of intensified crust-pressures, the faults were in many places overcast northwards or southwards, or in some oblique direction. The older fold-forms were locally thrown into steep knee-flexures, or new flexures developed, and new faults cut through them, usually with an inclination in one direction or another and the occurrence of local overthrusts.

Transverse vertical faults occurred at fairly regular intervals throughout the district, and at an advanced period, associated by the lecturer with the Dinaric (Peri-Adriatic) movements, cross-plication and cross-thrusting had been set up. The major fold-forms were of the nature of wide asymmetric anticlines with a steep western wing and a long gently-inclined eastern wing. The chief complications of the cross-movement occurred on the west side of these anticlines and in the areas of adjacent subsidence.

The vertical faults were in some cases overcast towards the west, or overcast folds formed and were fractured, and origin was given to the westward movement of thrust-masses.

Owing to recurrences of north-to-south pressures and to the marked inequalities of resistance, the later differential movements were extremely complex.

As a rule, gliding-planes developed within the thrust-masses themselves, and the upper layers tended to be carried farther forward than the lower.

A number of photographs of leading thrust-planes in the district and geological sections illustrated the relations of the thrust-masses of Pitschberg, on the north of Gröden Valley, Langkofl and Plattkofl, on the south of that Valley, and Buffaure, on the east of Fassa Valley. The horizontal displacements had not exceeded $2\frac{1}{2}$ kilometres.

Reference was then briefly made to the next important zone of east-to-west thrust-movement, which the lecturer had demonstrated in 1899 in the Boe Summit of Sella Massive. Reithofer had recently shown an extension of this thrust in the north of the group, where he believed it to be a 'relief' overthrust. Dr. Ampferer was of opinion that quite a number of these later overthrusts were of this character.

Still farther east, the lecturer showed in her geological map of Enneberg the occurrence of another zone of east-to-west thrusts

on the east of the Lower Enneberg and St. Vigil area, a zone associated with overthrusts in the extensive tract of dolomite-rock between Enneberg and Ampezzo.

March 20th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc.,
F.R.S., President, in the Chair.

The following communications were read:—

1. 'Some South Australian Algal Limestones in Process of Formation.' By Sir Douglas Mawson, O.B.E., B.E., D.Sc., F.R.S., F.G.S.

This contribution serves to record three different types of limestone now actually in process of formation, under the influence of plant-growth occurring in the south-eastern region of South Australia.

The locality is but slightly raised above sea-level and quite flat, but for a series of old vegetated calcareous sand-dunes which extend in parallel formation across the country, thus interfering with the drainage and determining low swampy intervening areas. It is an area of almost horizontal late Tertiary limestone.

A remarkable development of limestone-‘biscuits’ occurs at ‘Biscuit Flat’, a locality which is inundated in winter, but dries out in summer. The deposition of the calcium carbonate producing these forms is determined by the activities of blue-green algæ.

At a point near the coast, but isolated from the sea, are permanently inundated areas forming lakes of greater or less salinity. In Lake Karatta, one of these, an exuberant growth of algæ occurs, among which forms of *Lithothamnion* are conspicuous. Feeding upon the algæ are abundant shrimp-like crustaceans. A veritable reef of algal limestone is building out into the lake, comparable on a small scale with a fringing coral-reef.

Lakelets recently cut off from the Coorong, an arm of the sea, which usually dry up more or less completely during the summer months, are floored with a thick deposit of what is known locally as ‘pipe-clay.’ This proved to be a fine pulverulent deposit of calcium carbonate, somewhat dolomitized, evidently deposited from the saturated waters of the lakes during the spring season by the concentrating process of evaporation abetted by the presence of minute blue-green algæ.

2. ‘The Unroofing of the Dartmoor Granite, and an Outline of the Distribution of its Detritus in the Sediments of Southern England.’ By Arthur W. Groves, Ph.D., M.Sc., D.I.C.

A systematic outline mineralogical survey has been made of the sediments of Southern England, from the base of the Permian in Devon (Watcombe Clay) up to the Lenham Beds of the North Downs, in search of detrital minerals of the Dartmoor Granite. The work is based on the very detailed descriptions which have

been published by Dr. A. Brammell and others on the heavy mineral assemblages of the major granite-masses of Devon and Cornwall. Although it has been found possible to distinguish to a fair extent between the detritus from the various granites, the danger of confusing detrital material from Cornish granites with that from Dartmoor in the sediments of the South of England is largely obviated by the fact that detritus from the Cornish granites does not appear to have gone east of Dartmoor to any very appreciable extent, and that there are comparatively few post-Carboniferous sedimentary strata west of Dartmoor.

For the sake of brevity, no reference is made in the paper to those horizons in which Dartmoor detritus was not found.

The minor intrusions above the granite were being rapidly eroded in Permo-Triassic times, but there is no evidence of the actual granite being exposed at that period. The minerals of the pneumatolytic and contact-zones of the minor intrusions consanguineous with the granite were distributed in large quantity east and north-east of the Dartmoor area, but no evidence of them was found in the Slapton outlier.

No proof has been obtained of direct derivation of detritus from the Dartmoor Granite in the Jurassic rocks.

The earliest evidence of the exposure of the granite is in late Wealden times. Aptian yields mostly negative evidence. Throughout Upper Cretaceous times—particularly during the Selbornian epoch—the Dartmoor Granite contributed enormous quantities of detritus to the sediments of Southern England, reaching as far afield as Kent and Oxfordshire, and perhaps farther.

The Thanet Sand is barren, and the Reading Beds yield but very scanty evidence. The London Clay appears to be barren, except in West Dorset. Dartmoor detritus is present again in large quantities in the Bagshot Beds of Devon and Dorset, but east of the New Forest the evidence of it is obscured by increasing quantities of material from Armorica. The higher Eocene strata have yielded negative evidence.

The Oligocene of the Isle of Wight also yielded negative evidence.

The Aquitanian deposits of the Bovey and Petrockstow basins are, as already shown by Prof. P. G. H. Boswell, mainly derived from the Dartmoor Granite.

The Cornish Pliocene was largely derived from the Cornish granites. The St. Keverne outlier is mainly derived from the Falmouth and Bodmin masses, and yields no evidence of Dartmoor detritus.

A number of new occurrences of dumortierite are recorded in the paper.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

INDEX TO VOL. VII.

- ABERRATION** effect, on the, on straight-line reproduction, 441.
- Acceleration**, on the theory of absolute, 434.
- Acids**, on the size of the molecules of fatty, 940.
- Acoustic performance** of a disk driven by a coil in a radial magnetic field, on the, 1011.
- Adamson (J.)** on precision measurements of X-ray reflexions from crystal powders, 507.
- Adsorption** at the surface of binary liquid mixtures, on, 142.
- Air-flow** around a circular cylinder, on the, 253.
- Alexander (Prof. L. M.)** on the distribution of electrons in atoms, 517.
- Alkali metals**, on the spectra of, excited by active nitrogen, 729.
- Alloys**, on a new method of measuring the electrical resistance of, 662.
- Alternating current theory**, on a new transformation in, 477.
- Alty (Prof. T.)** on the influence of a high-potential direct current on the conductivity of an electrolyte, 153.
- Aluminium**, on the influence of hydrogen on the arc spectrum of, 312; on the absorption of X-rays by, 353.
- smoke particles, on the constitution of, 1107.
- Amalgams**, on the magnetic susceptibility of some, 145.
- Ammonia**, on the attachment of electrons to the molecules of, 277; on the Raman effect in, 744.
- Anand (C.)** on liquid drops on the same liquid surface, 247.
- Antimony smoke particles**, on the constitution of, 1106.
- Antimony-copper alloys**, on the magnetic susceptibility of, 150; on the Hall effect and other properties of, 161.
- Arc**, on the electric, in mixed gases, 1085.
- spectra, on the influence of hydrogen on the, of metals, 312.
- Arsenic smoke particles**, on the constitution of, 1106.
- Atoms**, on three-dimensional motion of an electron in the field of non-neutral, 31; on the distribution of electrons in, 517.
- Audition**, on the theory of, 477.
- Awbery (J. H.)** on heat flow when the boundary condition is Newton's law, 1143.
- Backhurst (I.)** on the absorption of X-rays from 0.63 to 2 Å.U., 353; on the effect of stress upon the X-ray reflexions from tungsten wire, 981.
- Baffle**, on the effect of a finite, on the emission of sound by a double source, 537.
- Bailey (Prof. V. A.)** on the attachment of electrons to the molecules HCl and NH₃, 277.
- Band (W.)** on the theory of absolute acceleration, 434; on Whitehead's and Einstein's laws of gravitation, 1183.
- Banerji (D.)** on the duration of contact between the pianoforte string and a hard hammer, 345.
- Barkla (Prof. C. G.)** on superposed X-radiations, 737.
- Barlow (Dr. H. M.)** on the electron theory of metals, 459.
- Bastings (L.)** on the temperature coefficient of gamma-ray absorption, 337.
- Bedford (L. H.)** on the e.m.f. of thermal agitation, 774.
- Beryllium**, on the spectrum of, 197.
- Beta-rays**, on the action of, on colloids, 86; on the waves associated with, 405.
- Binary liquid mixtures**, on adsorption at the surface of, 142.
- alloys, on the magnetic susceptibility of some, 145.

- Bismuth smoke particles, on the constitution of, 1108.
- Bohr-Heisenberg's uncertainty conditions, on, 1187.
- Bolometer, on the vacuum, 1067.
- Bond (Dr. W. N.) on the magnitude of non-dimensional constants, 719; on the frequency-distribution of examination marks, 1135; on certain molecular lengths measured by an optical lever, 1163.
- Books, new :—Collected Papers of Sir Jagadis Chunder Bose, 420; Macconochie's Thermodynamics Applied to Engineering, 420; Lorentz's Vorlesungen über Theoretische Physik an der Universität Leiden, 421; Kohlrausch's Wien-Harms Handbuch der Experimentalphysik, 421; Bowen's The Evolution of the Igneous Rocks, 634; Annual Tables of Constants and Numerical Data, 636; Birtwistle's The Principles of Thermodynamics, 636; Jellinek's Lehrbuch der Physikalischen Chemie, 637; Fisher's Statistical Methods for Research Workers, 638; Wien Harms Handbuch der Experimentalphysik, 638; Kingzett's Chemical Encyclopædia, 639; Honda's Magnetic Properties of Matter, 640; Collected Researches, National Physical Laboratory, 640; Thomson's Beyond the Electron, 750; Knopp's Theory and Application of Infinite Series, 750; Lyman's The Spectroscopy of the Extreme Ultra-Violet, 751; Travers's The Discovery of the Rare Gases, 751; Mather's Old Mother Earth, 752; Morse's Bibliography of Crystal Structure, 752; Jolley's Alternating Current Rectification, 898; Tolman's Statistical Mechanics, 898; Haas's Materiewellen und Quantenmechanik, 899; Lind's The Chemical Effects of Alpha Particles and Electrons, 899; Rideal and Taylor's Catalysis in Theory and Practice, 899; Richardson's Sound, 900; Crennell and Lea's Alkaline Accumulators, 900; Caven and Cranston's Symbols and Formulæ in Chemistry, 901; Turnbull's The Theory of Determinants, Matrices, and Invariants, 901; Becker's Untersuchungen zur Quantentheorie von Louis der Broglie, 902; Schrödinger's Four Lectures on Wave Mechanics and Collected Papers on Wave Mechanics, 902; de Broglie and Brillouin's Selected Papers on Wave Mechanics, 902; Bragg's Introduction to Crystal Analysis and The Structure of an Organic Crystal, 1096; Revision of Rowland's Preliminary Table of Solar Spectrum Wave-lengths, 1198; The Collected Works of J. Willard Gibbs, 1199; Wilson's Modern Physics, 1200; Sir J. J. Thomson and G. P. Thomson's The Conduction of Electricity through Gases, 1200; Eddington's The Nature of the Physical World, 1201; Eisenhart's Non-Riemannian Geometry, 1201; Haas and Hill's Introduction to the Chemistry of Plant Products, 1202.
- Bose (Prof. S. N.) on the beryllium spectrum in the region λ 3367–1964, 197.
- Bourgin (Dr. D. G.) on the propagation of sound in gases, 821.
- Bradley (R. S.) on adsorption at the surface of binary liquid mixtures, 142; on the lattice energy of LiH and the normal potential of H⁻, 1081.
- Brentano (Dr. J.) on precision measurements of X-ray reflexions from crystal powders, 507; on the application of a valve amplifier to the measurement of X-ray and photoelectric effects, 685.
- Brindley (G. W.) on the distribution of charge in the chlorine ion in rocksalt, 616; on the refractivity of gaseous compounds, 891.
- Bromwich (Dr. T. J. I'a.) on the phenomena of projected electrons, 470.
- Brönsted (J. N.) on the separation of isotopes, 631.
- Brown (W. L.) on groups of electrons in the Geissler discharge, 17.
- Browning (Dr. H. M.) on a complex pendulum driven by two pendulums having commensurate periods, 721.

- Buxton (A.) on the aberration effect on straight-line reproduction, 441.
- Cadmium, on the influence of hydrogen on the arc spectrum of, 212; on the energy of dissociation of molecules of, 555.
- and mercury vapours, on flutings in the absorption spectrum of a mixture of, 565.
- oxide, on the lattice constants of, 507.
- Cæsium, on the spectrum of, excited by active nitrogen, 733.
- Calcium nitrate, on the heat of solution of, 241.
- Calculus, on an extension of Heaviside's operational, 1153.
- Carbon, on the influence of hydrogen on the arc spectrum of, 312; on the spectrum emitted by, under bombardment, 706.
- Carrington (Dr. H.) on critical stresses for tubular struts, 1063.
- Carruthers (G. H.) on the application of Talbot's law to photo-electric cells, 792.
- Ceric hydroxide sols, on the action of ionizing radiations on, 86.
- Cerium, on the ionization potential of, 286.
- Chapman (Prof. S.) on the thermal diffusion of rare constituents in gas-mixtures, 1.
- Charlesworth (Prof. J. K.) on the South Wales end-moraine, 758; on the glacial geology of the Derbyshire dome, 759.
- Chlorine ion, on the distribution of charge in the, in rocksalt, 616.
- Cho (D. E. T.) on the three-electrode vacuum-tube oscillator, 1038.
- Chromium echelette gratings for infra-red investigations, on, 742.
- Clarkson (Dr. W.) on the intensities of some Fe^+ multiplets, 98; on the spectral phenomena of spark discharges, 322.
- Coblentz (W. W.) on the Raman spectra of scattered radiation, 203.
- Colloids, on the action of ionizing radiations on, 86.
- Condenser-telephone, on the, 115.
- Conductivity, on the influence of a high-potential direct current on the, of an electrolyte, 153; on the measurement of, by oscillating circuits, 567.
- Constants, on the magnitude of non-dimensional, 719.
- Coolman (C.) on a supposed limitation of the second law of thermodynamics, 504.
- Copper, on the action of ionizing radiations on colloidal, 86; on the absorption of X-rays by, 353.
- Copper-magnesium and copper-antimony alloys, on the magnetic susceptibility of, 150; on the Hall effect and other properties of, 161; on an X-ray investigation of the, 1113.
- Copper smoke particles, on the constitution of, 1102.
- Corona discharge in neon, on the, 632.
- Cox (H. L.) on the effect of stress upon the X-ray reflexions from tungsten wire, 981.
- Crew (Prof. H.) on the influence of a hydrogen atmosphere upon the arc spectra of certain metals, 312.
- Critical temperature, on the coefficient of cubical expansion of liquids and, 887.
- Crowther (Prof. J. A.) on the action of ionizing radiations on colloids, 86.
- Crystal detectors, on the effect of ultraviolet and X-rays on, 866.
- photographs, on the interpretation of X-ray, 373.
- powders, precision measurements of X-ray reflexions from, 507.
- structure of solid methane, on the, 761.
- Cupric chloride, on the heat of solution of, 236.
- Cylinder, on the air-flow around a, 253.
- Davies (W. G.) on the magnetic susceptibility of some amalgams and binary alloys, 145.
- Davis (Dr. A. H.) on the transmission of sound through partitions, 1050.
- Davison (Dr. C.) on the eleven-year and nineteen-year periods of earthquake frequency, 580.
- Diamonds, on the artificial preparation of, 488.
- Dielectric constants of imperfect insulators, on the, 985.
- Diffusion, on the thermal, of rare constituents in gas-mixtures, 1.

- Discharge-tube, on the control of current in a, 106.
- Disk, on the acoustic performance of a, driven by a coil in a radial magnetic field, 1011.
- Double refraction, on the dispersion of, in quartz, 80.
- Drops, on liquid, on the same liquid surface, 247.
- Dust figures, on the formation of Kundt's tube, 523.
- Dysprosium, on the ionization potential of, 286.
- Earhart (R. F.) on the control of current in a discharge-tube by means of a magnetic field, 106.
- Earthquake frequency, on the eleven-year and nineteen-year periods of, 581.
- Echelette gratings, on chromium, for infra-red investigations, 742.
- Edgeworth (Lt.-Col. K. E.) on frequency variations of the triode oscillator, 200.
- Einstein's law of gravitation, on, 1183.
- Elastic bodies, on the contact between two, pressed together, 453.
- Elasticity, on the method of Ritz for the solutions of problems in, 332.
- Electric arc, on the, in mixed gases, 1085.
- current, on the control of the, in a discharge-tube, 106.
- Electrical discharges, on high-frequency, in gases, 586, 600.
- resistance, on a new method of measuring the, of alloys, 662.
- Electrolysis, on, with a mercury cathode, 951.
- Electrolyte, on the influence of a high-potential direct current on the conductivity of an, 153.
- Electromagnetic field of an electron, on the, 425.
- Electromotive force of thermal agitation, on the, 774.
- Electron theory of metals, on the, 459.
- Electrons, on groups of, in the Geissler discharge, 17; on three-dimensional motion of, in the field of a non-neutral atom, 31; on the attachment of, to the molecules HCl and NH₃, 277; on the relation between free, and their waves, 405; on the electromagnetic field of, 425; on the phenomena of projected, 470; on the thermodynamical properties of, 493; on the distribution of, in atoms, 517; on two-dimensional periodic orbits of, 783.
- Elements, on regularities in the table of, 691.
- Emeléus (Dr. K. G.) on groups of electrons in the Geissler discharge, 17.
- Energy-frequency spectrum of static and of telegraph signals, on the, 176.
- Engines, on the thermal efficiency of standard cycles for internal combustion, 386.
- Ether, on the separation of thorium from uranium by, 670.
- Ethyl alcohol, on the heats of solution of some salts in, 209.
- Europium, note on, 1008.
- Evans (Prof. E. J.) on the Hall effect and other properties of the copper-antimony series of alloys, 161.
- Examination marks, on the frequency-distribution of, 1135.
- Expansion, on the coefficient of cubical, of liquids and critical temperature, 887.
- Page (A.) on the air-flow around a circular cylinder, 253.
- Fairclough (N.) on the vacuum bolometer, 1067.
- Ferrous sulphate solutions, on the action of X-rays on, 129.
- Fluids, on the steady motion of viscous, incompressible, 641.
- Frequency-distribution of examination marks, on the, 1135.
- Fricke (H.) on the action of X-rays on ferrous sulphate solutions, 129.
- Friction, on a molecular theory of, 905.
- Gadolinium, on the ionization potential of, 286.
- Gallium amalgams, on the magnetic susceptibility of, 145.
- Gamma-ray absorption, on the temperature coefficient of, 337.
- Ganguli (A.) on the hydrolytic adsorption by humic acid, 317.
- Gases, on the thermal diffusion of rare constituents in mixtures of, 1; on high-frequency discharges in, 586, 600; on the Raman effect in,

- 744; on the propagation of sound in, 821; on the electric arc in mixed, 1085.
- Gaseous compounds, on the refractivity of, 891.
- molecule, on the change that a, may undergo between two consecutive collisions, 53.
- Gatty (C.) on the dielectric constants of imperfect insulators, 985.
- Gehman (S. D.) on the measurement of conductivities by means of oscillating circuits, 567.
- Geissler discharge, on groups of electrons in the, 17.
- Geological Society, proceedings of the, 422, 753, 903, 1202.
- Geometrical radiation problem, note on a, 275, 1092.
- George (Dr. W. H.) on the interpretation of X-ray crystal photographs. 373.
- Gershun (A.) on uniformly diffused light through two apertures, 419.
- Gold, on the absorption of X-rays by, 353.
- amalgams, on the magnetic susceptibility of, 145.
- smoke particles, on the constitution of, 1103.
- Goldsbrough (Dr. G. R.) on the method of Ritz for the solution of problems in elasticity, 332.
- Goldstein (R. F.) on the constant of mass action, 205, 1193.
- Gordon (Mrs. M. M. O.) on the structure of the Western Dolomites, 1202.
- Gratings, on chromium echelette, for infra-red investigations, 742.
- Gravitation, on Whitehead's and Einstein's laws of, 1183.
- Green (C. B.) on the control of current in a discharge-tube by means of a magnetic field, 106.
- Green (Dr. G.) on the condenser telephone, 115.
- Gregory (Prof. J. W.) on the geological history of the Atlantic Ocean, 759.
- Grids, on the use of photographic, 373.
- Grime (G.) on the copper-magnesium alloys, 1113.
- Groves (Dr. A. W.) on the Dartmoor granite, 1205.
- Gupta (Dr. M. M. S.) on superposed X-radiations, 737.
- Hall effect, on the, of the copper-antimony series of alloys, 161.
- Hamada (H.) on the spectra of alkali metals excited by active nitrogen, 729.
- Harlow (F. H.) on the thermal expansions of mercury and vitreous silica, 674.
- Harris (F. C.) on the dispersion of double refraction in quartz, 80.
- Harrison (Dr. T. H.) on the application of Talbot's law to photo-electric cells, 792.
- Hayman (Dr. R. L.) on high-frequency discharges in helium and neon, 586.
- Heat flow when the boundary condition is Newton's law, on, 1143.
- Heats of solution, on the, of some salts in water and ethyl alcohol solutions, 209.
- Heaviside's operational calculus, on an extension of, 1153.
- Helium, on high-frequency discharges in, 586.
- excitation, on the Raman effect by, 858.
- Hevesy (Prof. G.) on the separation of isotopes, 631.
- Heyrovsky (Prof. J.) on electrolysis with a mercury cathode, 951.
- Higab (Dr. M. A.) on three-dimensional motion of an electron in the field of a non-neutral atom, 31; on two-dimensional periodic orbits in the field of a non-neutral, 733.
- Higgs (A. J.) on the attachment of electrons to the molecules HCl and NH₃, 277.
- Higham (F.) on the petrology of the basal complex of Jamaica, 903.
- High-frequency radiation, on the absorption of, 841.
- High-potential direct current, on the influence of a, on the conductivity of an electrolyte, 153.
- Hill (F. J.) on the size of the molecules of fatty acids, 940.
- Hoare (F. E.) on the platinum thermometer temperature scale, 384.
- Houstoun (Dr. R. A.) on the temperature of radiation and its photographic action, 1153.
- Humic acid, on the hydrolytic adsorption by, 317.

- Hydrogen, on the influence of, on the arc spectra of metals, 312; on the ionization of, by its own radiations, 970; on the normal potential of, 1081.
- chloride, on the attachment of electrons to the molecules of, 277; on the Raman effect in, 744.
- Indium amalgams, on the magnetic susceptibility of, 145.
- Infra-red investigations, on chromium echelette gratings for, 742.
- Insulators, on the dielectric constants of imperfect, 985.
- Internal combustion engines, on the thermal efficiency of standard cycles for, 386.
- Ionization, on the, of hydrogen by its own radiations, 970.
- potentials of the rare earth elements, on the, 285.
- Ionizing radiations, on the action of, on colloids, 86.
- Ions, on the radiometer effect of positive, 70.
- Iron, on the intensities of some multiplets in the arc and chromosphere spectra of, 98.
- smoke particles, on the constitution of, 1103.
- Irons (E. J.) on the formation of Kundt's tube dust figures, 523; on the effect of constrictions in Kundt's tube, 873.
- Irregular motions, on the analysis of, 176.
- Isotopes, on the separation of, 631.
- J phenomenon, on the, 737.
- Jackson (W.) on the effect of ultra-violet and X-rays on crystal detectors, 866.
- Jeffcott (Prof. H. H.) on the thermal efficiency of standard cycles for internal combustion engines, 386; on the nature and form of the contact between two elastic bodies pressed together by a given force, 453.
- Jones (Prof. O. T.) on the Yellowstone Cañon, 755.
- Jowett (Dr. A.) on the glacial geology of the Derbyshire dome, 759.
- Keeping (E. S.) on the magnetic susceptibility of some amalgams and binary alloys, 145.
- Kenrick (Dr. G. W.) on the analysis of irregular motions, 176.
- Kleeman (Dr. R. D.) on the change that a gaseous molecule may undergo between two consecutive collisions, 53; on the constant of mass action, 206; on the thermodynamical properties of the electron, 493.
- Knipp (Prof. C. T.) on the radiometer effect of positive ions, 70.
- Kundt's tube, on the effect of constrictions in, 873.
- dust figures, on the formation of, 523.
- Lanthanum, on the ionization potential of, 286.
- Lattey (R. T.) on the dielectric constants of imperfect insulators, 985.
- Lattice energy of LiH, on the, 1081.
- Lead smoke particles, on the constitution of, 1106.
- Leech-Porter (J. A. H.) on the influence of a high-potential direct current on the conductivity of an electrolyte, 153.
- Light, on the intensity of the scattered, from an unpolarized beam, 204; on uniformly diffused, through two apertures, 419, 1093.
- scattering in liquids, on the theory of, 160.
- Liquid drops on the same liquid surface, on, 247.
- mixtures, on adsorption at the surface of binary, 142.
- Liquids, on the theory of light-scattering in, 160; on the Raman effect in some organic, 597.
- Lithium hydride, on the lattice energy of, 1081.
- Littler (T. S.) on the transmission of sound through partitions, 1050.
- Loud-speaker, on the coil-driven, 1011.
- McLachlan (Dr. N. W.) on the acoustic performance of a vibrating rigid disk driven by a coil situated in a radial magnetic field, 1011.
- McLennan (Prof. J. C.) on the crystal structure of solid methane, 761.
- Magnesium, on the influence of hydrogen on the arc spectrum of, 312.
- and copper alloys, on the magnetic susceptibility of, 150; on an X-ray investigation of the, 1113.

- Magnetic field, on the control of current in a discharge-tube by means of a, 106.
- susceptibility of some amalgams and binary alloys, on the, 145.
- Mahajan (L. D.) on liquid drops on the same liquid surface, 247.
- Manganese carbonate, on the lattice constants of, 507.
- phosphide, on the specific heat of, 125.
- smoke particles, on the constitution of, 1108.
- Marsh (Dr. J. K.) on the rare earths associated with uraninites, 1005.
- Martyn (Dr. B. F.) on frequency variations of the triode oscillator, 1094.
- Mass action, on the constant of, 205, 206, 1193.
- Matley (Dr. C. A.) on the crater of Papanajan, 754; on the basal complex of Jamaica, 903.
- Mawson (Sir D.) on South Australian algal limestones, 1205.
- Mazza (L.) on the crystal structure of nickel, 301.
- Meksyn (D.) on the electromagnetic field of an electron, 425; on the, motion of a particle as a statistical problem, 1187.
- Mendelejeff's table, on, 691.
- Mercury, on the superficial properties of, 418; on flutings in the absorption spectrum of a mixture of the vapours of, and cadmium, 565; on the thermal expansion of, 674.
- cathode, on electrolysis with a, 951.
- Metals, on the electron theory of, 459.
- Methane, on the crystal structure of solid, 761.
- Mica, on the measurement of the thickness of thin sheets of, 1163.
- Millikan (Dr. C. B.) on the steady motion of viscous incompressible fluids, 641.
- Milne (Prof. E. A.) on a geometrical radiation problem, 275.
- Misciatelli (Dr. P.) on the separation of thorium from uranium by means of ether, 670.
- Molecular lengths, on the measurement of, by an optical lever, 1163.
- Molecular theory of friction, on a, 905.
- Molecules, on the change that gaseous, may undergo between two consecutive collisions, 53; on the size of the, of fatty acids, 940.
- Moran (W. G.) on simple methods of purifying radium emanation, 399.
- Morris-Jones (W.) on the copper-magnesium alloys, 1113.
- Morse (S.) on the action of X-rays on ferrous sulphate solutions, 129.
- Moving-coil loud-speaker, on the, 1011.
- Mukherjee (S. K.) on the beryllium spectrum in the region λ 3367-1964, 197.
- Multiplet spectra of iron, on the, 98.
- Nasini (A. G.) on the crystal structure of nickel, 301.
- Neodymium, on the ionization potential of, 286.
- Neon, on high-frequency discharges in 586; on the corona discharge in, 632.
- Nethercot (W.) on high-frequency discharges in gases, 600.
- Newbold (A. A.) on the spectrum emitted by a carbon plate under bombardment, 796.
- Newman (Prof. F. H.) on the electric arc in mixed gases, 1085.
- Nickel, on the crystal structure of, 301.
- Nitrogen, on the spectra of alkali metals excited by active, 729.
- Non-dimensional constants, on the magnitude of, 719.
- Norbury (Dr. A. L.) on a new method of measuring the electrical resistance of alloys, 662.
- Okubo (J.) on the spectra of alkali metals excited by active nitrogen, 729.
- Operational calculus, on an extension of Heaviside's, 1153.
- Optical lever, on the measurement of molecular lengths by a, 1163.
- Orbits, on two-dimensional periodic, in the field of a non-neutral, 783.
- Oscillating circuits, on the measurement of conductivities by, 567.
- Oscillator, on frequency variations of the triode, 200, 1094; on the three-electrode vacuum tube, 1038.

- Particles, on the motion of, on a rough sphere, 569; on the motion of a, as a statistical problem, 1187; on the constitution and density of, in precipitated smokes, 1097.
- Partington (Prof. J. R.) on the heats of solution of some salts in water and ethyl alcohol solutions, 209.
- Partitions, on the transmission of sound through, 1050.
- Pendulum, on a complex, driven by two pendulums, 721.
- Perucca (Prof. E.) on the superficial properties of mercury, 418.
- Photoelectric cells, on the application of Talbot's law to, 792, 812.
- effects, on the application of a valve amplifier to the measurement of, 685.
- Photographic action, on the temperature of radiation and its, 1139.
- Photographs, on the interpretation of X-ray crystal, 373.
- Pianoforte string, on the duration of contact between the, and a hard hammer, 345.
- Piccardi (Prof. G.) on the ionization potentials of the rare earth elements, 286.
- Platinum, on the absorption of X-rays by, 353.
- smoke particles, on the constitution of, 1106.
- thermometer temperature scale, on the, 384.
- Plummer (Dr. W. G.) on the crystal structure of solid methane, 761.
- van der Pol (Dr. B.) on a new transformation in alternating current theory, 477; on Heaviside's operational calculus for invariable systems, 1153.
- Porter (Prof. A. W.) on surface tension, 624.
- Positive ions, on the radiometer effect of, 70.
- Potassium, on the spectrum of, excited by active nitrogen, 733.
- chloride, on the heat of solution of, 222.
- thiocyanate, on the heat of solution of, 227.
- Praseodymium, on the ionization potential of, 286.
- Presad (K.) on a dynamical method for determining Young's modulus by bending, 548.
- Quartz, on the dispersion of double refraction in, 80.
- Radiation, on the absorption of high-frequency, 841; on the temperature of, and its photographic action, 1139.
- problem, note on a geometrical, 275, 946, 1092.
- Radiometer effect of positive ions, on the, 70.
- Radium emanation, on methods of purifying, 399.
- Raman (Prof. C. N.) on light-scattering in liquids, 153.
- Raman effect, on the, in some organic liquids, 597; on the, in gases, 744; on the, by helium excitation, 858.
- Rare earths, on the ionization potentials of the, 285; on the, associated with uraninites, 1005.
- Refractivity, on the, of gaseous compounds, 891.
- Reynolds (Prof. S. H.) on the carboniferous section at Cattybrook, 424.
- Ritz, on the method of, for the solution of problems in elasticity, 332.
- Rocksalt, on the distribution of charge in the chlorine in, 616.
- Rolla (Prof. L.) on the ionization potentials of the rare earth elements, 286.
- Samarium, on the ionization potential of, 286.
- Sandeman (Dr. E. K.) on the e.m.f. of thermal agitation, 774.
- Sandford (Dr. K. S.) on the erratic rocks of the Oxford district, 753.
- Scandium, note on, 1008.
- Scattered light from an unpolarized beam, on the, 204.
- radiation, on the Raman spectra of, 203.
- Seta (Dr. L.) on the artificial preparation of a diamond, 488.
- Seth (J. B.) on liquid drops on the same liquid surface, 247.
- Shotton (F. W.) on the geology of the country round Kenilworth, 423.
- Silica, on the thermal expansion of, 674.
- smoke particles, on the constitution of, 1107.
- Silver, on the absorption of X-rays by, 353.
- smoke particles, on the constitution of, 1100.

- Simunek (Dr. R.) on electrolysis with a mercury cathode, 951.
- Smith (Dr. S.) on the carboniferous section at Cattybrook, 424.
- Smokes, on the constitution and density of particles in precipitated, 1097.
- Sodium, on the spectrum of, excited by active nitrogen, 731.
- thiocyanate, on the heat of solution of, 230.
- Soils, on the acidity of, 317.
- Solar radiation, on the measurement of, 1067.
- Solution, on the heats of, of some salts in water and ethyl alcohol solutions, 209.
- Soper (Dr. W. E.) on the heats of solution of some salts in water and ethyl alcohol solutions, 209.
- Sound, on the effect of a finite baffle on the emission of, by a double source, 537; on the propagation of, in gases, 821; on the transmission of, through partitions, 1050.
- Sound-tube, on the effect of constrictions in Kundt's, 873.
- Spark discharges, on the spectral phenomena of, 322.
- Spath (Dr. L. F.) on the landslide at Rocken End, 422.
- Specific heat, on the, of manganese phosphide, 125.
- Spectra, on the arc and chromosphere, of iron, 98; on the band, of cadmium and zinc, 555; on flutings in the absorption of a mixture of mercury and cadmium vapours, 565; on the, of alkali metals excited by active nitrogen, 729.
- Spectrum, on the, emitted by carbon under bombardment, 706.
- Sphere, on the motion of a particle on a rough, 569.
- Stars, on the limiting density in, 63.
- Static disturbances, on the energy-frequency spectrum of, 176.
- Stein (W. S.) on the radiometer effect of positive ions, 70.
- Stephens (E.) on the Hall effect and other properties of the copper-antimony series of alloys, 161.
- Stevenson (A. F.) on the motion of a particle on a rough sphere, 569.
- Stiles (W. S.) on the intensity of the scattered light from an unpolarized beam, 204; on Talbot's law, fatigue, and non-linearity in photoelectric cells, 812.
- Straight-line reproduction, on the aberration effect on, 441.
- Stoner (Dr. E. C.) on the limiting density of white dwarf stars, 63; on the absorption of high-frequency radiation, 841.
- Stress, on the effect of, upon the X-ray reflexions from tungsten wire, 981.
- Stresses, on the, between elastic bodies pressed together, 453; on critical, for tubular struts, 1063.
- Strömholm (Prof. D.) on some regularities in the table of elements, 631.
- Struts, on critical stresses for tubular, 1063.
- Strutt (Dr. M. J. O.) on the effect of a finite baffle on the emission of sound by a double source, 537.
- Surface-tension, notes on, 624.
- Talbot's law, on the application of, to photoelectric cells, 792, 812.
- Telegraph signals, on the energy-frequency spectrum of, 176.
- Telephone, on the condenser, 115.
- Terbium, on the ionization potential of, 286.
- Thattle (V. N.) on the coefficient of cubical expansion of liquids and critical temperature, 887.
- Thermal agitation, on the e.m.f. of, 774.
- diffusion of rare constituents in gas-mixtures, on the, 1.
- efficiency of standard cycles for internal combustion engines, on the, 386.
- expansions of mercury and vitreous silica, on the, 674.
- Thermodynamics, on the second law of, 504.
- Thermometer, on the platinum, temperature scale, 384.
- Thomson (Prof. G. P.) on the rays associated with beta-rays and the relation between free electrons and their waves, 405.
- Thomson (J.) on the ionization of hydrogen by its own radiations, 970.
- Thorium, on the separation of, from uranium by ether, 670.

- Three-electrode vacuum-tube oscillator, on the, 1033.
- Tin amalgams, on the magnetic susceptibility of, 145.
- smoke particles, on the constitution of, 1109.
- Tomlinson (G. A.) on a molecular theory of friction, 905.
- Townsend (Prof. J. S.) on high-frequency discharges in gases, 600.
- Triode oscillator, on the frequency variations of the, 200, 1094.
- Tungsten smoke particles, on the constitution of, 1108.
- wire, on the effect of stress upon the X-ray reflexions from, 981.
- Ultraviolet rays, on the effect of, on crystal detectors, 866.
- Uraninites, on the rare earths associated with, 1005.
- Uranium, on the separation of thorium from, by ether, 670.
- Vacuum bolometer, on the, 1067.
- Vacuum-tube oscillator, on the three-electrode, 1033.
- Valve amplifier, on the application of a, to the measurement of X-ray and photoelectric effects, 685.
- Venkateswaran (S.) on the Raman effect in some organic liquids, 597.
- Viscous fluids, on the steady motion of, 641.
- Walmsley (H. P.) on the constitution and density of particles in precipitated smokes, 1091.
- Walsh (J. W. T.) on a geometrical radiation problem, 1092; on uniformly diffused light through two apertures, 1093.
- Water, on the heats of solution of some salts in, 209; on the dielectric constant of, 1001.
- Weatherby (B. B.) on the measurement of conductivities by means of oscillating circuits, 567.
- White dwarf stars, on the limiting density in, 63.
- Whitehead's theory of absolute acceleration, on Dr. A. H., 434; law of gravitation, on, 1183.
- Whitmore (B. G.) on the specific heat of manganese phosphide, 125.
- Winans (Dr. J. G.) on the energies of dissociation of cadmium and zinc molecules, 555; on flutings in the absorption spectrum of a mixture of mercury and cadmium vapours, 565.
- Wood (R. G.) on the distribution of charge in the chlorine ion in rock-salt, 616.
- Wood (Prof. R. W.) on chromium echelette gratings on optical flats for infra-red investigations, 742; on the Raman effect in gases, 744; on the Raman effect by helium excitation, 858.
- Wright (C. E.) on a geometrical radiation theorem, 946.
- X-radiation, on the action of, on colloids, 86; on superposed, 737.
- X-ray crystal photographs, on the interpretation of, 373.
- effects, on the application of a valve amplifier to the measurement of, 685.
- investigation of the copper-magnesium alloys, on an, 1113.
- reflexions from crystal powders, precision measurements of, 507; on the effect of stress on the, from tungsten wire, 981.
- X-rays, on the action of, on ferrous sulphate solutions, 129; on the absorption of, from 0.63 to 2 Å.U., 353; on the effect of, on crystal detectors, 866.
- Young's modulus, on a dynamical method for the determination of, 548.
- Ytterbium, on the ionization potential of, 286.
- Zinc, on the influence of hydrogen on the arc spectrum of, 312; on the energy of dissociation of molecules of, 555.
- carbonate, on the lattice constants of, 507.

END OF THE SEVENTH VOLUME.

DATE DUE

UIC 3-DAYS

APR 28 1996

RET'D. PER APR 25 1996